THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

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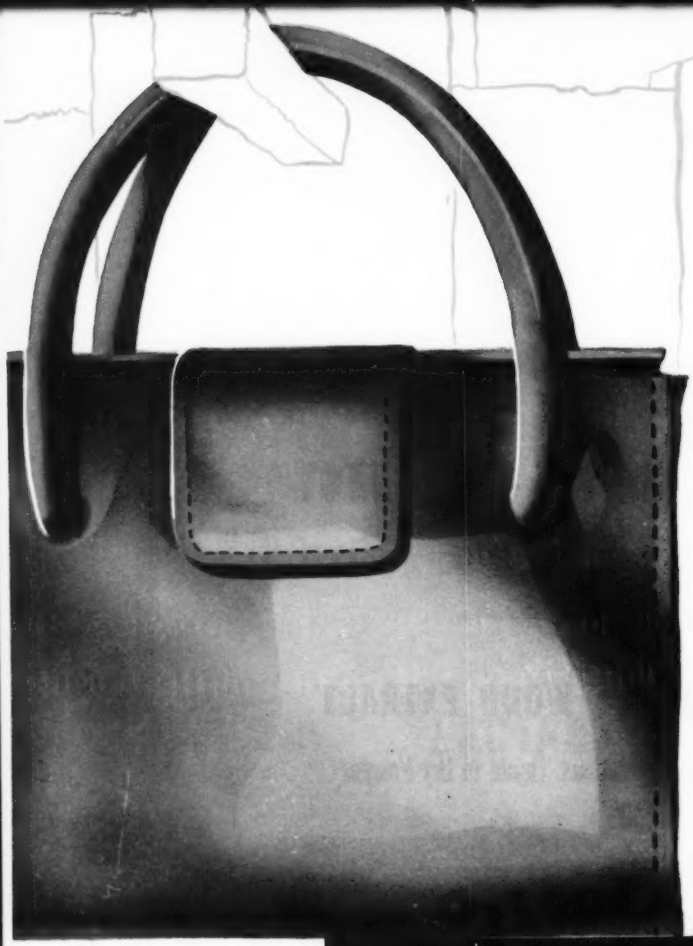

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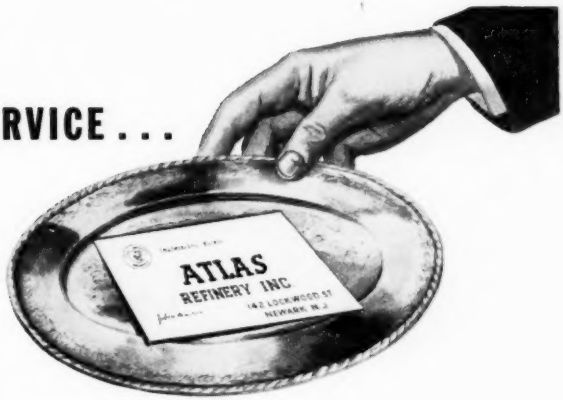

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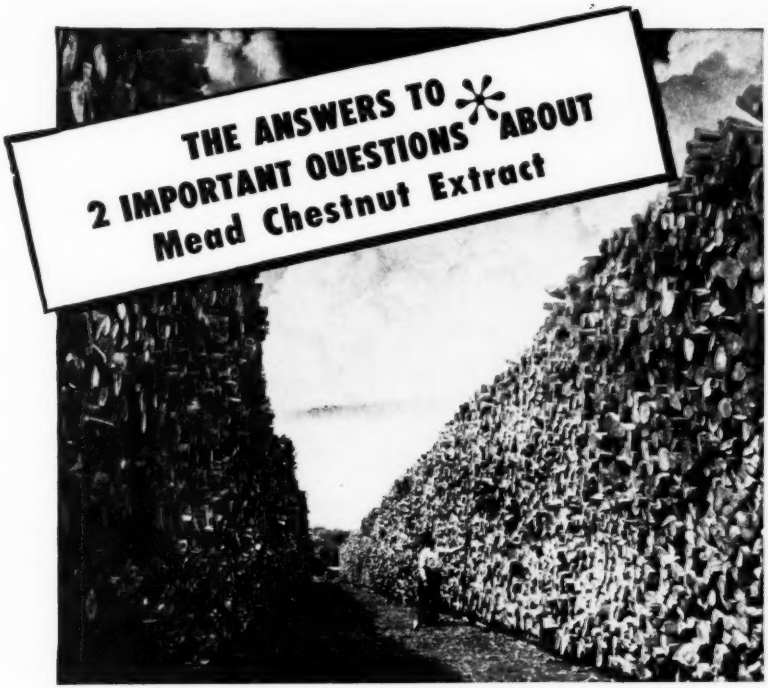

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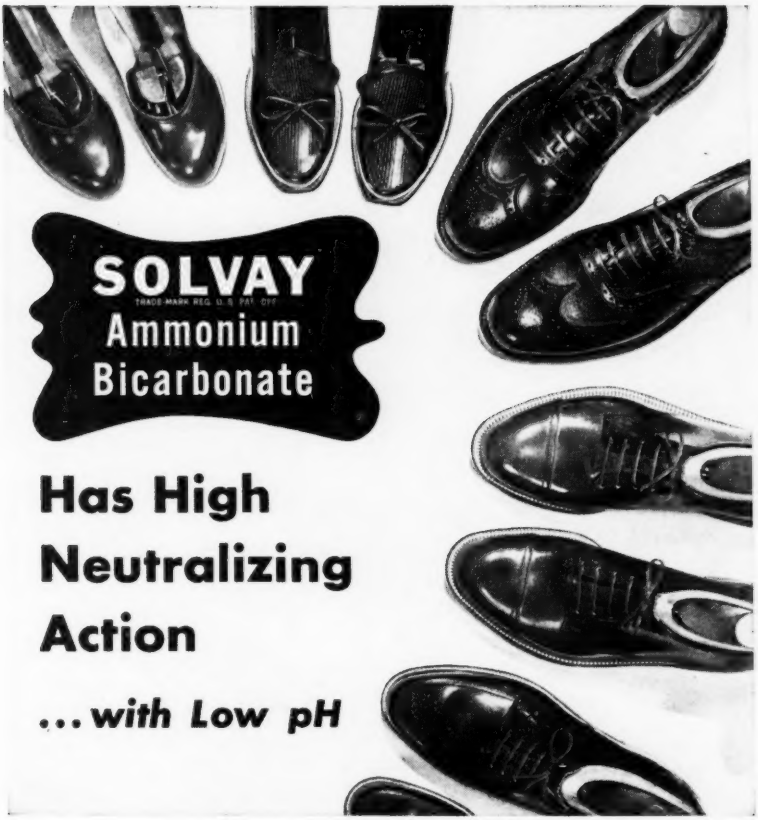

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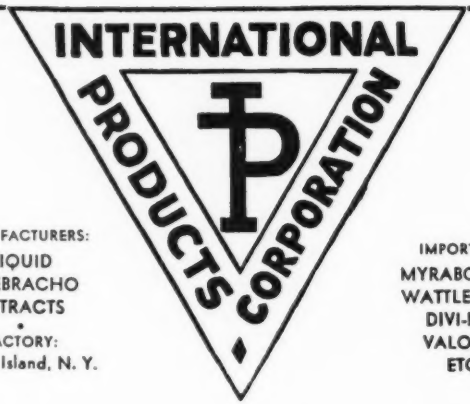

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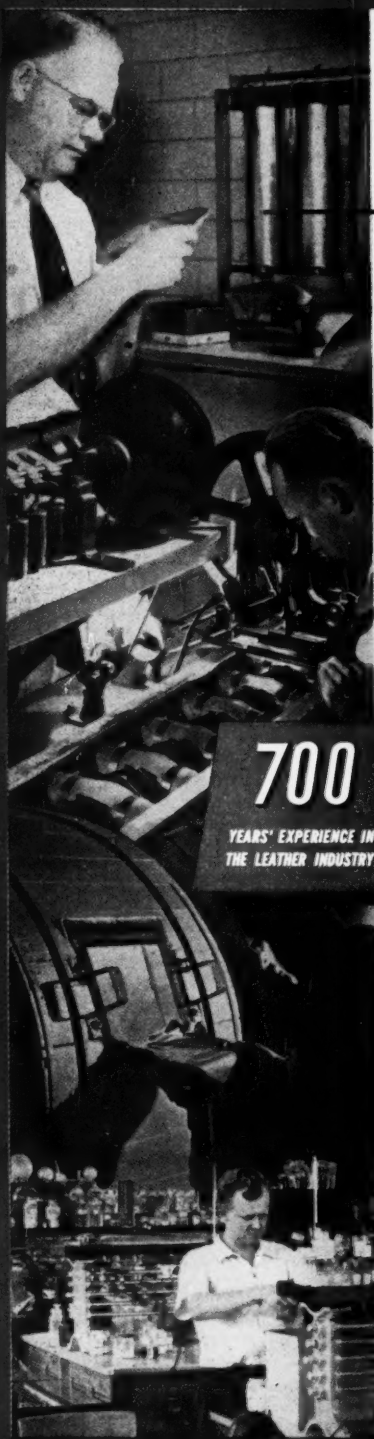

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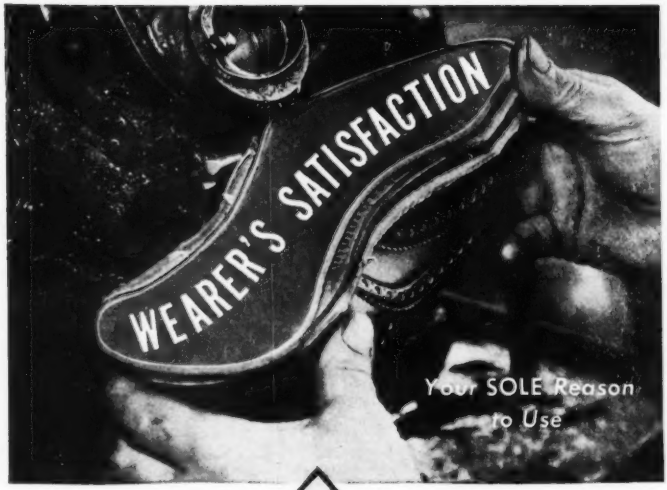

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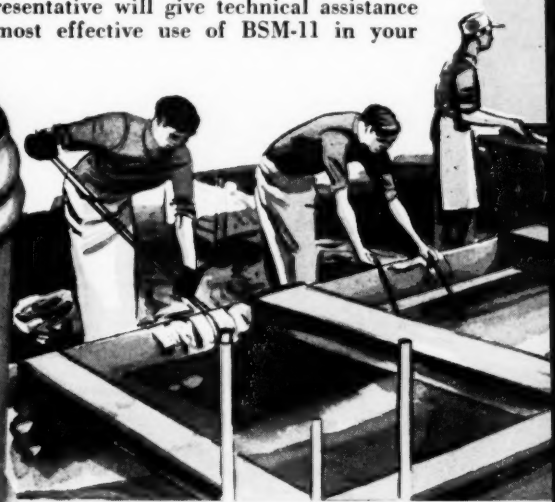

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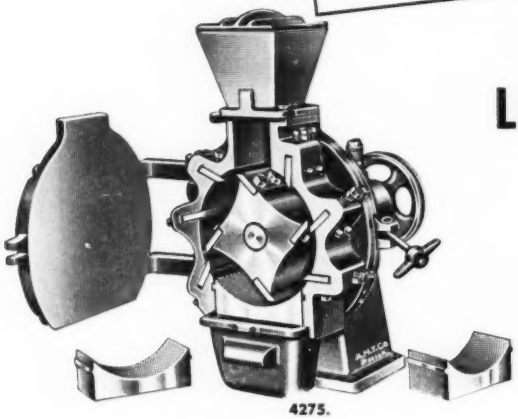

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The French School of Tanning and The Research Institute for the Leather Industries*

By Dr. Paul Chambard

The French School of Tanning was founded in the year 1899 by the General Leather and Hide Syndicate of France. At that time it was located at the Institute of Chemistry at the University of Lyon. Up to the year 1945 the management had been in the hands of Professor L. Meunier. His place has been taken by Professor P. Chambard who, at that time was, the associate director.

In the year 1922, there was attached to the French School of Tanning a research laboratory under the direction of Professor Chambard. This research laboratory was attended by chemical engineers, most of whom were former students of the French School of Tanning or of the School of Industrial Chemistry at Lyon. These students wished to continue their studies in preparation of their doctoral dissertations. Thus, more than twenty dissertations, concerning subjects of interest to the leather industries, were prepared and were accepted by the examining board of the university.

This research laboratory was not subsidized. The candidates for the doctorate who attended it, were not on a salary basis. On the contrary, they turned over to the university all academic rights connected with their studies. Thus, it was not possible to force upon them a certain subject of particular practical interest for the leather industry.

It was not until 1940 that the necessity of such work became evident to the leading persons of the tanning industry. At that time, the Research Institute for the leather industries was founded. This organization was endowed by subsidies from manufacturers. This made it possible to hire specialized students and to direct their studies toward a well defined goal.

*Presented at the Golden Jubilee Meeting of the A.L.C.A. in Cincinnati, Ohio, June 9, 1953.

Although administratively separated from the French School of Tanning, the Research Institute for the leather industry, nevertheless, has remained closely connected with it. We shall see later the advantages of this connection.

These two organization, School and Institute, underwent a rapid development after the year 1944. There were 34 students in 1938. This number increased to 70 in 1950. In addition, a preparatory course has been created at the School, so that the number of students has risen to a total of 85.

For its part, the Research Institute had to increase its personnel rapidly to almost 30. Under these condition, the premises which the organization occupied at the Chemical Institute, became too small. In 1942, the management of the School of Tanning decided to undertake the construction of buildings designed to shelter the French School of Tanning, the Research Institute, and an experimental laboratory equipped with machinery and the material necessary for the operation of small scale tanning processes.

In fact, it was decided to maintain close cooperation between the Research Institute and the School of Tanning, a cooperation which had undisputable advantages. The engineers of the Research Institute can, in a very effective way, collaborate in the instruction of the school by means of courses and discussions concerning problems with which they were familiar. The teachers at the school also can collaborate in research work and, furthermore, the expensive equipment of the experimental laboratory can, at the same time, be used for practical work by the students to try out tanning methods studied and developed in the laboratories of the Research Institute.

These buildings have been financed by benevolent gifts from French industrialists in the leather industry. The buildings are not completely finished; however, they are sufficiently advanced so that the School of Tanning and the Research Insitute have been installed there since 1951. The School has there its laboratories and lecture rooms, equipped as originally planned. The experimental laboratory has been installed temporarily in the large basement. Also in the basement there are set up two laboratories, one for analytical purposes, and one for research. The photographs which I am showing you give an idea of the actual lay-out.

Activities of the Research Institute

At the time of the founding of the Research Institute for the Leather Industry there was a great shortage of raw materials in France. The country lacked especially vegetable tans and chrome salts. It was only natural that the Research Institute was urged to suggest a remedy for this state of affairs. Its first investigations concerned the astringency of vegetable tans. It succeeded in designing a suitable method of reducing the astringency of chestnut extract in such a way that the speed of penetration into the hide

tissue was accelerated. This permitted replacement of quebracho extract which was unobtainable.

Then, studies followed concerning the economy of chrome products. These studies resulted in mixed tanning methods, quinone-chrome and especially formaldehyde-chrome, whereby the amount of chrome could be reduced to 750 grams of chromium oxide per 100 kilos of raw unpickled hide, yielding at the same time, satisfactory hide material.

Production without chrome salts of hide products with the appearance of box-calf was also studied. A liquor was suggested for the tanning with iron salts, or better, mixed tanning with formaldehyde-iron and quinone-iron. Tanning with iron salts was also used to replace vegetable tanning.

When the commercial relations between the civilized countries were re-established, then these manufacturing methods disappeared completely, with the exception of two, namely:

1. "Sweetening", or in other words "reducing" the astringency of chestnut extract.
2. Preparation of iron-tanned leathers of the so-called "oiled leather" type for upper shoe leather.

These leathers are designed for the manufacture of heavy-duty footwear, especially army boots.

The so-called "sweetened" chestnut extract with its rapid penetration, has remained popular in France. Its combination with sulfited quebracho extract gives very good results in the manufacture of vegetable tanned leather. There have been published numerous papers on the astringency of vegetable tanning extracts and the possibility of its modification. I do not think that I have to come back to this subject.

The formaldehyde-chrome combination mixture has been abandoned with good reason. It yields merchandise of good appearance and softness but the leather products are brittle, and their tearing resistance is just about half as good as that of chrome leather.

The manufacture of box-calf by tanning with iron salts is more expensive and more delicate than that by means of chrome tanning. It is difficult to control. The leathers obtained with it are inferior to those made with chrome tanning, in regard to appearance, softness and firmess. Therefore, at the present state of our knowledge, it does not seem to be desirable to attempt to replace chrome tanning with this process of manufacture.

Present Activities of the Research Institute

At the present time, these are the principal subjects studied at the Research Institute.

Tanning with silicic acid (silica tanning)

Tanning with ferric salts (iron tanning)

Conservation of fresh, salted skins and the control of salt stains
Determination of the quality of shoe leathers.

I am going to give here a brief review of the various problems and wish to indicate the state of development of each one of them at the time of writing this report.

Silica tanning

Tanning with silicic acid is a relatively old invention. In the year 1916, A. T. Hough claimed a patent in which the process is clearly defined. The advantage of this tanning method is evident, because it uses a very cheap raw material, sodium silicate, which is obtained from silicious sands which are abundant on the surface of the earth.

This tanning method consists mainly of a treatment of the skin with acid sols of silicic acid. The hides absorb silicic acid and are converted into white and soft leather.

Although its inventor, A. T. Hough, spent years of constant effort, this tanning process could not be perfected satisfactorily, and it has not been adopted by the industry. This failure must be attributed to the instability of the silicic acid sols. This acid can exist in sol-form only in solutions which are extremely acid (pH, at the most, 1.0). Even under these conditions the silica forms with itself insoluble polymers by a condensation reaction. The sol becomes more or less rapidly opalescent, the viscosity increases and, finally, a gel is formed. This polymerization is more rapid with higher concentration of the sol, with weaker acidity, and with higher temperature. The insolubilization of the silica starts frequently during the tanning process and the latter cannot be finished properly. Even if this does not take place, the silica particles become rapidly too large. They deposit themselves in great quantity upon the surface of the leather, making it harsh-grained and brittle.

At the Research Institute, we have taken up again the investigation of such tanning, at first with the cooperation of Mrs. Jullien, then of Miss Lasserre. During her work, Miss Lasserre made us familiar with work done by H. Kraut (Berichte der Deutschen Chemischen Gesellschaft **64**, 1709, [1931]). This paper indicated that sols were obtained in which the molecular weight is at a minimum at pH 3.2, when starting from sodium metasilicate with ratio $SiO_2 : Na_2O = 1 : 1$, and when mixing a solution of this salt with a mixture of hydrochloric and acetic acids. At pH 3.2, the solution contains monosilicic acid.

In such sols, at pH 3.2, condensation is slow. H. Kraut found that there was obtained after 5 days disilicic, and after 8 days decasilicic acid. From then on the determination of molecular weight is not possible. Sodium metasilicate ($SiO_2 : Na_2O = 1 : 1$) is commercially available in crystalline form, and, therefore, is a well-defined product. The other forms of sodium

silicate which are available on the market are concentrated solutions with higher ratios $SiO_2 : Na_2O$.

It is necessary for the preparation of silica-tanning baths to neutralize the alkalinity of the sodium silicate completely. Therefore, it seemed of interest to turn to products with a higher ratio $SiO_2 : Na_2O$. We believe that this is one of the difficulties which have been encountered in silica tanning by those authors who preceded us in our work.

By starting from the data given above and by using crystallized sodium metasilicate, we were able to obtain sols with such stability that they did not turn into gels for several weeks, whereas sols made with other sodium silicates of poorly defined composition were not stable for a few days, or even hours.

The acidity of these sols (pH 3.2) is very convenient for their application. The tanning effect can be produced regularly and safely, even on heavy hides.

However, this working method does not overcome entirely the difficulties of silica tanning. The fixation of silica upon the hide is still too heavy. The leathers thus produced contain 20% of it or more. Such high amounts of inorganic tanning agents make the leather brittle.

We think that we can avoid this difficulty by applying to the raw hide pretanning operations capable of blocking partly the fixation of the silicic acid. This investigation is under way, and certain pretanning treatments have proven to be effective.

The leather samples which we show you here give an idea of what we were able to accomplish so far. A theoretical study of tanning with silicic acid has been undertaken by Miss Lasserre, and will be published soon. We can already now draw the conclusion that the silicic acid is not only fixed to the free carboxylic functions of the protein but also to the peptide linkages. In any case, silica tanning should be considered as real tanning and not as a deposit of insoluble silica between the skin fibers. The shrinking temperature of completely silica-tanned leathers actually increases to 90° C.

Tanning with ferric salts

This tanning method has already been considered for a long time. The first investigations in this respect go back to the same time as those concerning chrome tanning (1860). However, while the latter progressed rapidly, iron tanning was not successful in the industry. A great deal of research has been carried out in regard to this tanning method. We are not going to discuss all of it but mention especially work done by Çasaburi who recommended the addition of citric or tartaric acids to the tanning liquors, and work done by Röhm & Haas. Among other adjuvants, this latter company recommended the use of sodium phosphate.

It is our belief that the failure of tanning with ferric salts is caused, on the one hand, by the instability of basic ferric complex compounds which are

present in the tanning liquors, and, on the other hand, in the durability of leather tanned with basic ferric sulfate.

The ferric sulfate solution can be made basic with sodium carbonate in the same way as chromic sulfate. Its color turns then from light yellow into reddish brown. Without precipitation of ferric hydrate, at average iron concentrations, it is possible to obtain a basicity of 30° Schorlemmer. This basic solution is not stable. It changes rapidly, and ferric hydrate is precipitated with a strongly acid, yellow liquor on top. The presence of raw hide in this solution accelerates this reaction. The tanning starts out in a normal way but, before it is finished, the liquor flocculates. Accordingly, the main problem is the stabilization of basic tanning liquors. This can be carried out either by the addition of acids with hydroxyl functioning groups (citric, tartaric acid, or lactic acid), or by the addition of dicarboxylic acids, such as phthalic, oxalic, and adipic acids.

The effect of these various salts upon tanning is measured by the following determinations.

1. The shrinking temperature of the leather obtained.
2. The swelling of the leather coming out of the tanning bath. The intensity of the dehydration effect produced by the tanning is the reciprocal of the swelling.

The following table gives the results obtained with various salts.

Trial No.	Salts added to the tanning liquor	Shrinking temperature	Swelling expressed as % water of dy leather	% hide substance of the dry leather (100% basis)	% ashes of dry leather (100% basis)	% Fe_2O_3 in dry leather (100% basis)
1	phosphate	68	133	75.5	17.8	16.8
2	phthalate	77	122	70.1	16.5	15.9
3	tartrate	77	134	77	15.9	14.9
4	adipate	74	132	71	18.7	17.4
5	lactate	63	136	79.4	13.2	13
6	oxalate	65	142	79.2	12.8	12.6
Blank	——	60	160			

In all trials:
Fe = 4.50 g per 100 cc. of bath
Monosodium phosphate = 0.96 g/ 100 cc. of bath
Stabilizing salts = 0.2 molecules per 2 Fe
The blank consists of untanned hide powder and swelled in water at pH 4

We see that all these salts produce a stabilizing effect but that the tanning effect varies considerably. The tanning effect is very weak in the case of phosphates, lactates and oxalates but it is quite noticeable with tartrates and adipates, and best in the case of phthalates. We also observe that there

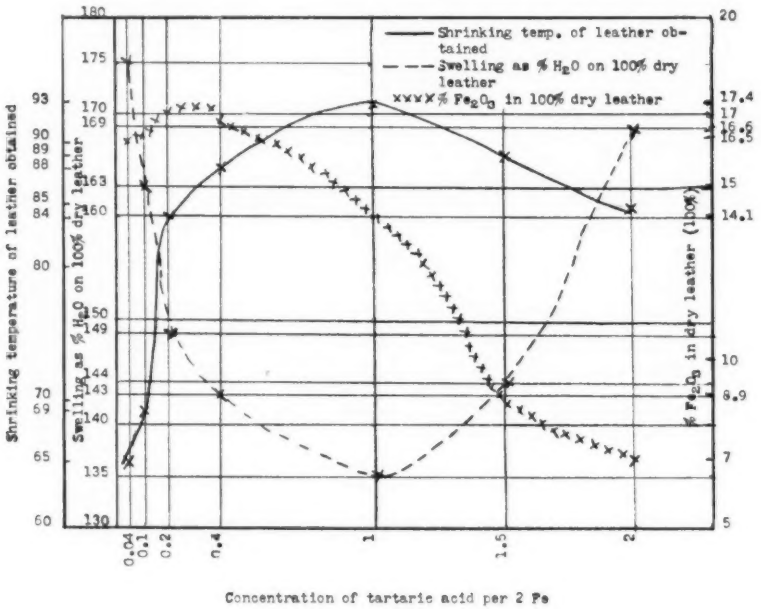
appears to be no relation between the amount of iron absorbed and the produced tanning effect.

We carried out a special study on tartrates in which we varied the concentration of these salts in the tanning liquor. The results are shown in the following graph.

We see that the tanning effect is highest for a certain concentration of sodium tartrate, namely 1 molecule per 2 Fe. This tanning effect is the same whether we measure the reduction in swelling or the shrinking temperature of the leather. There is no relation to the amount of absorbed iron oxide.

The low solubility of phthalic acid prevents a similar study with this acid or its salts. However, the data in the above table show that there is a strong tanning effect.

These considerations enabled us to offer to the French tanners a new method of tanning.


Shrinking temp. of leather obtained
Swelling as % H_2O on 100% dry leather
xxxx % Fe_2O_3 in 100% dry leather
Shrinking temperature of leather obtained
Swelling as % H_2O on 100% dry leather
% Fe_2O_3 in dry leather (100%)
Concentration of tartaric acid per 2 Fe

Leathers obtained by means of iron tanning have always been considered poor in regard to durability, and, actually, those produced before 1940, changed rapidly during storage. This was thought to be the result of a defect of iron tanning. This helped to discredit this tanning method.

We have recognized that this is not the case. Leathers obtained with the aid of iron tanning are generally very acid and it is the excessive acidity

which causes the change in them. These changes do not take place when there is sufficient neutralization. However, this neutralization is not always possible. Leather tanned with basic ferric sulfate alone cannot be neutralized beyond pH 3. Its stability range lies between pH 1 and pH 3. Leather obtained by using tartaric acid salts can undergo a somewhat higher neutralization without losing its properties. But the most stable leathers, by far, are those which contain complex compounds of phthalic acid. They can be neutralized to pH 4.5, and can be stored without any alteration. We kept samples of such leathers for almost 10 years. There were no signs of any changes in them.

The work with ferric salts has been carried out during a time of shortage in mineral and vegetable tanning materials. In most cases, the tanning proved to be inferior to chrome tanning or vegetable tanning and has been discontinued. However, there is one case which has shown an undeniable advantage and can hope for a certain future, and that is the manufacture of leather for heavy-duty shoe uppers and especially for military boots. It must be noted that these leathers receive, after tanning, a thorough treatment with oil, that is fish oil. These oils undergo in the leathers an internal, rapid oxidation, catalized by the presence of iron. The result is that these leathers receive, in addition to iron tannage, a real oil tannage. This is the reason why they possess the especially important properties of softness, firmness and impermeability.

The samples which I am going to show you will give you an idea of the nature of this tanning, which, by the way, has been approved by the military services.

An important improvement in the process of iron salt tanning can be realized by the use of gluconic acid. This acid can now be made at a price that permits its application. It is now being studied at the Research Institute.

Quality and conservation of the raw hide: Conservation by means of salting

The Research Institute for the Leather Industry has been working on this problem for 2 years. It uses for this purpose its laboratories for microbiology under the direction of Mr. Boidin, assistant in vegetable biology at the University and also head of the experimental laboratory of the research institute. Practical trials of salting and conservation can be carried out. This is done by purchasing each year, for the tanning experiments by the pupils, about one hundred and fifty calfskins.

In 1952, trials were carried out to verify the statements of German authors that the addition of sodium carbonate to the salts used in salting permits a better conservation of the hides. For this purpose, pilot-plant trials were carried out and batches of 20 hides were salted as follows:

1. With salt alone.

2. With salt to which had been added 2.5% of sodium carbonate and beta-naphthol.
3. With salt to which had been added 2.5% of anhydrous sodium carbonate.

The trials were carried out during the three hottest months of the year, June, July, and August. They are described in an early issue of "Bulletin des Documents Scientifiques et Techniques des Industries du Cuir".
The trials indicated that:

(1) the addition of sodium carbonate to the salt prevents positively the formation of little yellowish, hardened spots on the flesh side, the so-called "salt stains".

(2) the addition of sodium carbonate to the salt *does not prevent* red and violet discolorations upon the flesh (red or violet heat).

(3) the addition of an antiseptic agent, e.g. beta naphthol, prevents the formation of red or violet heat.

The pH of the salted hides in the presence of sodium carbonate is in the range from 7.2 to 7.5, without sodium carbonate in the range from 6.8 to 7.0. When sodium carbonate produces an antiseptic effect, then this effect is not caused by the alkalinity. It is not certain that the salt stains on the flesh are of bacterial origin. If sodium carbonate has a suppressing effect upon bacterial growth, this can be due to a modification in the aerobic conditions. In fact, when there are produced slight amounts of acid at the beginning of the fermentation of the hide, this acid will react with the sodium carbonate and create a carbonic acid atmosphere which remains between the hides as long as the bundles or stacks are undisturbed.

This year, we intend to carry out trials in which we replace the sodium carbonate with sodium bicarbonate, with and without the addition of antiseptics other than beta naphthol. If the effect of sodium carbonate is due to the formation of anaerobic matter, sodium bicarbonate should be at least equal in effect.

We should mention here that W. Freudenberg, who recommended the use of sodium carbonate, specified that this salt must contain some naphthalene. It is possible that this compound plays an effective role as an antiseptic.

Determination of the quality of shoe leathers

Up to the beginning of this year there were no standards for the evaluation of the quality of shoe leathers. Certain organizations, especially the Military Services, in their specifications, have provided regulations concerning the conditions under which leather for army boots will be considered satisfactory. They are limited to analytical data.

Since 1951, the French tanning industry has felt itself to be severely threatened by the intensive competition to leather by substitutes, such as rubber or materials based on rubber, or plastics.

This situation became more serious during the year 1952. At this time, the leaders in the tanning industry and those in the shoe industry realized that, in order to defend the existence of leather, it was of greatest importance to provide the best possible quality. They requested the Research Institute for the leather Industry to study specifications that would characterize good leather.

These studies concerned bottom leathers (sole leathers) and upper leathers. Only the specifications for sole leather have been published so far. We have thought that the results of a chemical analysis, in themselves, do not permit any valid conclusions in regard to quality. Some of these results, however, should be considered.

Chemical analysis

We distinguished between two kinds of sole leather, namely that for walking or outside leather, and insole leather, the roles of which are different in shoe economy. These sole leathers must have entirely different characteristics.

As far as the *outsole leather* is concerned, we have specified a maximum content of watersoluble matter of 18%, a maximum of mineral matter of 2%, and a maximum content of magnesium sulfate of 3% (as $MgSO_4$, $7H_2O$). I should mention that these data refer to 100% leather with zero per cent water content, and that the extraction of soluble matter is carried out at 118°–120° F.

The presence of a somewhat higher amount of soluble matter in a leather for outsoles contributes to the impermeability of this leather. We do not wish this quality in *insole leather*. On the contrary, the insole leather has to absorb the perspiration from the feet, and therefore, has to be very permeable to water. On the other hand, soluble matter is dissolved by the perspiration, and is transferred into the hide of the upper part of the shoe. Since the latter is chrome tanned, the soluble matter and especially soluble mineral matter, deteriorate it rapidly. This is the reason why we have reduced the amount of soluble matter in insole leather to 14% and specified that there must be not more than 1% of soluble mineral matter.

Physical and mechanical properties

These are much more important for the evaluation of the quality of leather than the results of chemical analysis. These are also more difficult to determine correctly. We limited ourselves to the study of only those properties that appeared important to us, but plan also to investigate others.

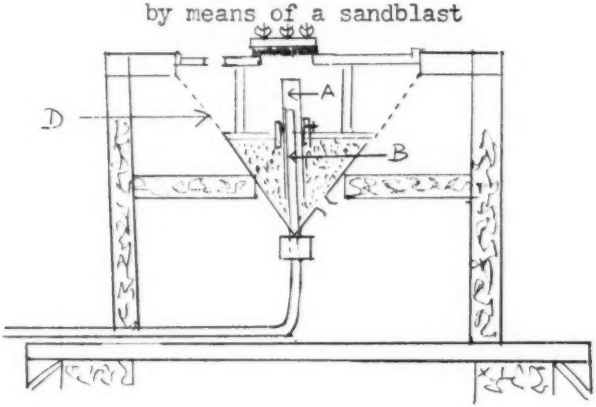
In the case of *outsole leather* we must consider the behavior toward water, and the wearing resistance.

There are two tests for the behavior toward water. There is the test for water absorption during 1 hour and during 24 hours. (We have fixed a maximum of 45% in 24 hours. The determination is carried out with the aid of the apparatus described by Kubelka). Then, there is the test of softening in water, where we determine mainly the pressure resistance of the leather in the dry and wet state. The best tannings are those in which the firmness is only slightly reduced after rewetting. It would take too long to give details of this determination. They may be found in a pamphlet which we published on this subject: "Label de qualité du Conseil National de Cuir" (Standard of quality by the National Leather Council).

The wearing resistance test is obviously one of greatest importance for the outsole. The determination of this property proved to be difficult. Most machines for the measurement of wearing resistance of leather are abrasion testers in which the leather is submitted to friction on an abrasive surface (grindstone or abrasive paper). The results obtained with different machines do not agree with each other. With certain machines it is difficult to get satisfactory agreement in successive tests on the same leather.

We have constructed a machine on an entirely different principle. This is not an abrasion tester but an erosion tester, in which the leather is exposed to a sandblast effect, causing wearing by erosion. The machine is calibrated by an erosion test on an aluminum disk, and the results are given in per cent resistance of the leather compared with that of aluminum.

Apparatus for the determination of
Wearing resistance of leather
by means of a sandblast



The apparatus which we constructed is not an abrasion machine but an erosion device (see figure). It consists mainly of a tube A with a diameter of

13 mm. in which there is another thin tube B. With the aid of the latter, we can blow in air under pressure. The lower end of the tube A descends into sand of certain grain size contained in the cloth bag D, which has a conical shape. The whole apparatus is enclosed in a box, closed at the upper end with a steel plate. This plate is provided with an opening in which we can place a round disk of the leather to be tested. The disk is fastened with the aid of 4 screws.

The axis of the two-tube system must be perfectly centered and go exactly through the center of this sample disk. The box has no bottom, but rests upon a larger box. The sidewalls of this box are perforated so that the air can be expelled after being filtered through wood fiber. This fiber will retain all of the sand that would eventually escape the apparatus.

When we send compressed air through the tube B under sufficient pressure, then the air stream takes up the sand and throws it violently against the leather disk. The sand falls back into the bag and may be used over again. Its level remains constant, so that the amount of sand and the velocity with which it is thrown against the leather remain constant as long as the pressure does not change.

We work under a constant pressure of 4 kilos per cm^2. The upper end of tube A is placed at 2 cm below the lower surface of the sample. Under these conditions we get complete wearing of the leather, namely perforation of the sample during time intervals which vary from 25 to 60 minutes, depending upon the erosion resistance of the leathers tested.

The erosion velocity can be expressed as follows:

(1) By measuring the weight loss of the leather per time unit

(2) By measuring the loss in thickness of the leather per time unit

(3) By measuring the time required to perforate the leather and expressing the result per millimeter thickness of the sample.

Our specifications for insole leather with entirely different qualities, are the following.

Minimum of water absorption

Minimum of tearing resistance, i. e. about 3 kilos per millimeter of thickness.

Minimum of tear-out resistance, i.e. about 11 kilos per millimeter of thickness

Minimum of permeability for water vapor (steam)

These determinations are carried out with the aid of known methods which I do not have to describe in detail.

The Research Institute for the Leather Industries has, besides the research laboratory, an analytical laboratory which carries out mainly analyses and plant control tests for the industry.

There is also a special laboratory for the preparation of hide powder for tan-analyses. Here, they prepare white hide powder for analysis by the "shake-method", chrome hide powder for analysis by the filter method, and finally hide powder for direct detanning, a method which permits us to obtain the same results as obtained by the "shake-method", but in a very short time and with less handling.

This laboratory can produce about 150 kilos of hide powder per month.

Received, June 10, 1953.

The Organic Chemistry of the Vegetable Tannins* A Half Century in Retrospect

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The tannins are amorphous substances, widely distributed in the wood, bark, leaves, and or roots of many members of the plant kingdom. They have been recognized from prehistoric times by their ability to convert putrescible skins and hides into durable leather; this use still accounts for perhaps the maior industrial use of these materials. The astringent properties of the tannins gave them a place in primitive materia medica, while the reaction of tannins and iron salts to form inks was well known to the alchemists. These properties still are responsible for minor uses of the tannins. Sequin [1] drew attention to the fact that tannins are precipitated by gelatin, and the haze problem in beer reflects a protein-tannin interaction. The ability of tannins to serve as colloidal stabilizers results in these materials finding industrial use in boiler water treatment and oil well drilling mud preparations. Though these substances have been industrially significant for centuries, it is only within the past half century that significant progress has been made in the elucidation of their structural chemistry. This review will endeavor to summarize this development of our knowledge. Especial emphasis will be devoted to the period since the publication of the review by Russell [2] in 1935.

THE STATUS OF OUR KNOWLEDGE IN 1900

At the start of this century, our knowledge of the chemistry of the vegetable tannins was limited to their classification and their decomposition products which result when they are decomposed by heat and acids. Procter [3] classified the tanning materials into catechol tannins, giving greenish-black colors with iron-alum and precipitating with bromine water, and the pyrogallol

*Presented at the Golden Jubilee Meeting of the A.L.C.A. in Cincinnati, Ohio, June 9, 1953.

tannins, giving a bluish-black with iron-alum and giving no precipitate with bromine water. He notes further that such phenolic structures as pyrogallol, phloroglucinol, pyrocatechol, resorcinol, gallic acid and ellagic acid may be formed from the tannins by the action of dry heat or acids. He also recognized the presence in the tannin molecule of such larger molecules as digallic acid, catechin, and possibly flavones or flavonols. He also noted that the tannins are probably often present as glucosides.

The quantitative method of analysis of extracts for the tannin content using the shake method with pre-chromed hide powder became an official international method in 1906. This method recognized the fact that no part of the known chemistry of the tannins except their ability to react with skin substance was able to characterize their value to the tanner.

The first third of the present century resulted in a very significant increase in our knowledge of the organic chemistry of the vegetable tannins. This developed from the work of Fischer [4], Freudenberg [5] Nierenstein [6] and Russell [2]. Each of these four men have published manuscripts which review this development. The next section of this paper will briefly review this extensive work.

Specific Structures Proposed for the Tannins

Perkins and Everest [7] classified the tannins in a manner which is suggestive of their structure:

1. Tannins related to the depsides; i. e., gallotannin.
2. Tannins related to diphenyldimethylolid; i. e., the ellagitannins.
3. Phlobatannins or catechol tannins.

Flinn [8] has reviewed the Freudenberg [9] classification of the tannins which further illustrates their structural chemistry:

A. Hydrolyzable tannins, in which the benzene nuclei are united in a larger complex by means of oxygen atoms and are split into simple components by acids and hydrolyzing enzymes.
   1. Mutual esters of phenol carboxylic acid or with hydroxy acids.
   2. Esters of phenol carboxylic acids with polyatomic alcohols and sugars.
   3. Glucosides of the gallotannins and ellagitannin type.

B. Condensed tannins, in which the nuclei are held together by carbon linkages and cannot be cleaved by acids and enzymes.
   1. Simple ketones, such as hydroxybenzophenones and hydroxyphenyl styryl ketones.
   2. The bulk of the commercial tannins, such as the phlobatannins or catechol tannins.

Fischer and his associates were chiefly concerned with the structural chemistry of gallotannin. Russell and his coworkers were interested in the synthesis of compounds considered to be analogous to the tannins, especially the phlobatannins and gallotannin. Freudenberg and Nierenstein were interested in the probable structural chemistry of both the hydrolyzable and condensed tannins.

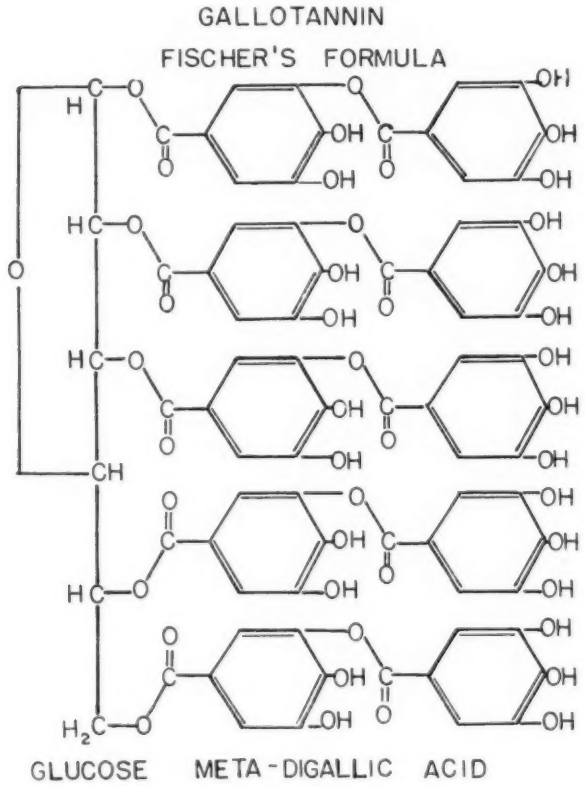


FIGURE 1.

The structure of gallotannin was the center of a vigorous literature controversy during the first third of this century. Fischer and Freudenberg[10] announced that gallotannin is a penta-digalloyl glucose. They purified commercial gallotannin by an alkaline extraction of an ethyl acetate solution of the tannin. This purified product hydrolyzed to yield 93.6 per cent gallic acid and 6.8 per cent glucose, in comparison to the theoretical value of 94.6

per cent gallic acid and 10.6 per cent glucose. The postulated structure to fit these data appears in Figure I.

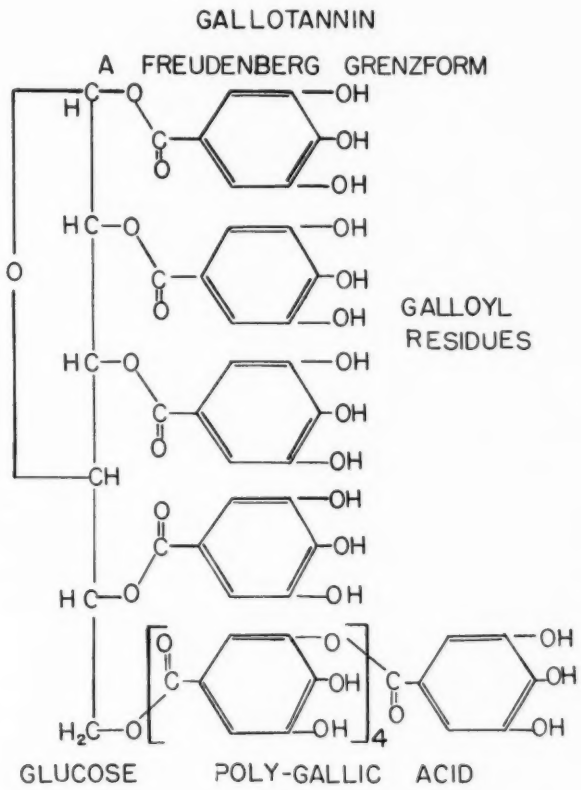


FIGURE II.

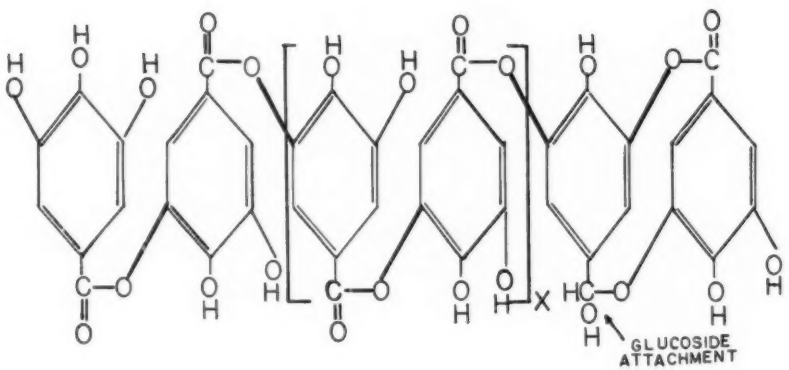
This postulated structure was supported by the synthesis of pentagalloyl alpha-glucose, pentagalloyl betaglucose, and the equivalent digalloyl esters by Fischer and Bergmann [11]. Despite these syntheses, however, it was not shown that any of the products were identical with gallotannin. In fact, Freudenberg [9] considers that it is possible that the glucose secondary alcoholic groups carry only one galloyl residue, while the primary alcohol carries a linear array due to hexagalloyl esterfication. Karrer, Salomon, and Peyer [12] further did not feel that there must always be ten galloyl residues in gallotannin, although they in general supported Fischer's hypothesis. A repre-

sentative Freudenberg grenzform to illustrate these hypotheses is shown in Figure II.

GALLOTANNIN

NIERENSTEIN'S FORMULA

(1935)



POLY-DIGALLIC ACID LEUCODIGALLIC ACID ANHYDRIDE

FIGURE III.

Nierenstein [6, 13], on the other hand states: "I do not regard glucose as an essential part of the gallotannin molecule, since we have found that by the action of yeast, it is possible to free gallotannin from glucose without destroying the gallotannin molecule. The view held by me is: gallotannin is polydigalloyl leucodigallic acid anhydride (see Figure III) as originally suggested by me in 1912, which may or may not exist in the form of a glucoside, to which we have assigned the name gallotannin-glucoside. The fact that gallotannin may be freed from glucose by the action of yeast finally disposes of the pentadigalloyl glucose formula of Fischer as opposed to my views on gallotannin."

Nierenstein seems to have modified the details of his structural formula between 1922 [14] and 1925 [15]. The chief difference in the two formulae is that the anhydride is shown between the terminal carboxyl group and a hydroxy group in the next to the last gallic acid residue in the 1925 article, while the 1922 article shows the anhydride between the terminal carboxyl group and a hydroxyl in the third from the last gallic acid residue.

Nierenstein's 1922 article lists five facts which indicate the correctness of this formula:

1. The formula explains the high molecular weight, the optical activity, and the low electrical conductivity of gallotannin.
2. The greater acidity of gallotannin to diazoacetic ester, in comparison to pyrogallol, is explained.
3. The mutarotation of gallotannin is consistent with the formula.
4. The phases in the formation of ellagic acid are consistent with the formula.
5. The formation of tetramethyl glucose on the hydrolysis of methylogallotannin is explained.

This latter point was developed by Nierenstein, Spiers, and Geake [16] who methylated gallotannin and synthetic pentagalloyl glucose with diazomethane. Hydrolysis of the products with glacial acetic acid yielded glucose with the synthetic pentagalloyl glucose, but tetramethyl glucose with gallotannin. Nierenstein [6] regards this observation as the most convincing evidence against the Fischer formula.

Mitchell [17] has published a colorimetric method to estimate pyrogallol, gallic acid, and gallotannin employing ferrous tartrate. He indicates that his results are more consistent with the Nierenstein formula than with the Fischer formula.

Despite Nierenstein's unequivocal rejection of the Fischer formula as recently as 1934, subsequent references generally accept the Fischer formula as correct. Thus, Russell [2] dismisses the Nierenstein formula with only this statement: "It must be pointed out, however, that Nierenstein (our reference 6, his reference 34) takes almost unqualified exception to Fischer's views and considers that gallotannin is a polydigalloyl leucodigallic acid anhydride, that may or may not be associated with glucose."

Russell, Tebbens, and Avery [18] note a grave deficiency in these earlier studies with respect to the proof of the tanning power of the synthetics. They note that the synthetic products were tested as gelatin precipitating agents, but that proof is not offered that they have tanning properties. They note that while tanning materials will all precipitate gelatin, all gelatin precipitants will not form leather. They rightly conclude that "the only safe, final, and reliable test for tanning properties is the making of a piece of leather."

Russell and his associates [18, 19] investigated the relationship between chemical constitution and the tanning effect for several esters of gallic acid. They state [18] that "it seems certain from Fischer's work that unaltered gallotannin from Chinese galls is penta-m-digalloylglucose; and it may be inferred that if this compound were prepared synthetically in sufficient quantity for testing, it would show leather forming properties. Although it

would be worthwhile repeating the synthesis of this compound from the point of view of general interest, the repetition of the synthesis of such a complex compound would serve no useful purpose from the point of view of the present research since much simpler compounds with good tanning properties are likely to be found."

These authors [19] first established that gallic acid, ethylene glycol, glycerol, d,l-erythritol, d-arabitol, sorbitol, and the methyl, ethyl, n-propyl, isopropyl, n-butyl, n-amyl, and n-hexyl gallates do not tan; i.e., do not make leather. In comparison to "pure gallotannin (tannic acid)," which is said to give a very good tannage, ethylene glycol digallate and glycerol trigallate gave a poor tannage; further, d, l-erythritol tetragallate, d-arabitol pentagallate, and mannitol and sorbitol hexagallates gave fair tannages. Further, beta-d-glucose penta gallate, d-mannose pentagallate, d-glucose diethylmercaptal penta-gallate, and aldehydo-d-glucose pentagallate were excellent tanning materials, forming leather strictly comparable, both for quality and color, to that given by natural gallotannin. In addition, the fully galloylated aldo-pentose, d-arabinose tetragallate, as well as alpha-methyl-d-glucoside tetra gallate had good leather forming properties.

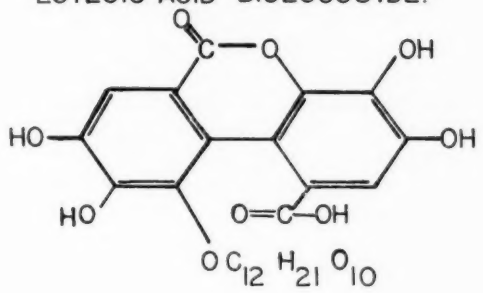
It is surprising to note that Russell and Tebbens [19] found that the fully galloylated ketohexose fructose pentagallate is not a tanning material, while an isomeric fully galloylated aldohexose (pyranose or aldehyde form) or an epimeric form was found to be good tanning material. They further note that both precipitate gelatin while only the aldohexose form produces leather. They did not speculate on the reason for this specificity. Further, this significant observation seems to have escaped attention by those studying tanning structure. An understanding of the reasons for this specificity would be informative in our knowledge of the mechanism of tannage. It also implies caution in any conclusions as to the identity of a synthetic product and a natural tannin unless very thorough identity studies have been made.

In summary, it seems to be proved beyond any reasonable doubt that pentagalloyl glucose does have tanning properties similar to gallotannin. However, the structural chemistry of gallotannin has not been shown to be based upon this synthetic model in the same convincing fashion. While the Fischer or probably Freudenberg concept seems to be the most logical, it also seems the Nierenstein's evidence must also be shown to be consistent with the galloyl glucose concept of the structure of the gallotannins. Modern techniques of physical organic chemistry should be applied to this very interesting problem.

The ellagitannins present a more complex structural chemistry which has not been as exhaustively studied as that for gallotannin. The practical tanner has long recognized that such tannin materials as myrobalans, valonea and divi-divi deposit "bloom" on the surface of leather. Further, at the beginning of this century, it was known that this "bloom" was ellagic acid.

COMPONENTS OF MYROBALAN TANNIN.

LUTEOIC ACID BIGLUCOSIDE.



CHEBULINIC ACID OR EUTANNIN

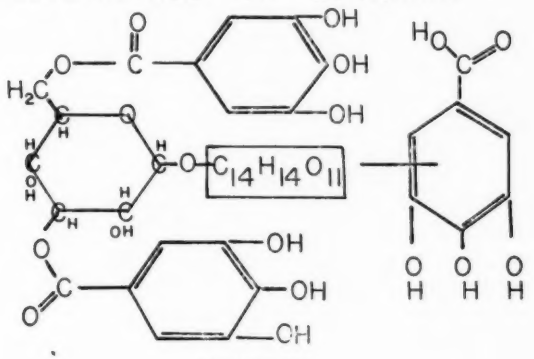


FIGURE IV.

Schiff[20] suggested the correct formula for ellagic acid in 1879 when he observed that it could be formed from meta digallic acid. Perkin and Nierenstein[21] synthesized it by the oxidation of two moles of gallic acid, using potassium persulfate and sulfuric acid. Further, they showed that ellagic acid is split by alkali to yield pentahydroxy diphenylmethylolid. Thus, ellagic acid was shown to be 3, 4, 3′, 4′ tetra hydroxy diphenyldimethylolid (by 1905). The work of the past fifty years has been concerned with the organization of ellagic acid and the other components to form the ellagitannins.

The composition of the tannins in myrobalans, the fruits of various terminalia species, has been shown to be heterogeneous through extensive structural studies during the past half century. Myrobalani—tannin and chebulinic

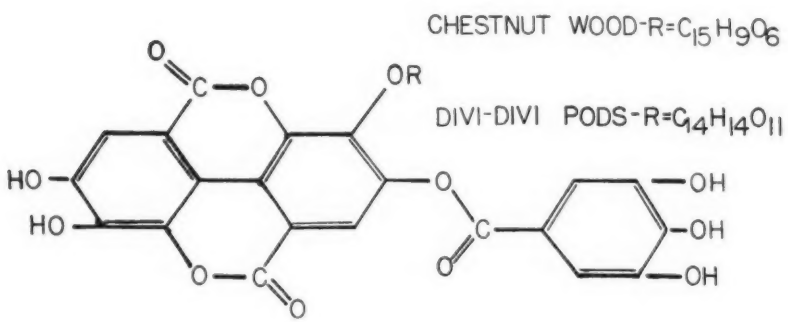
acid have been identified and considerable progress made toward structural characterization. These structures comprise Figure IV.

The chemical name of myrobalani-tannin is luteoic acid biglucoside, which can be hydrolyzed to yield first luteoic acid and finally ellagic acid. Nierenstein has studied this tannin extensively, presenting the structure given in Figure IV in 1935 [6]. It is interesting to note that Nierenstein [22] in 1911 found that luteoic acid and its glucoside precipitates gelatin, but that ellagic acid does not. More recently, Nierenstein and Potter [23] have confirmed the structure of myrobalani-tannin and shown its presence in quantities from 14 to 28 per cent in many sources of hydrolyzable tannin, including myrobalans, dividivi, algarobilla and valonea.

Chebulinic acid has long been known to contain glucose, gallic acid, and an unknown oxygen rich component. Freudenberg has studied the structure of chebulinic acid extensively and presented a tentative formulae in 1933 [5]. He concludes that the 3 and the 6 positions of the glucose are esterfied with gallic acid; the one and two positions on the glucose carry the oxygen rich "split acid" which carries another gallic acid residue. Schmidt, Heintzeler, and Mayer [24] have confirmed this structure except that they present a different elemental analysis for the "split acid". This latter formula is shown in Figure IV.

SOME HYDROLYZABLE TANNINS.

FORMULAE GIVEN BY FLINN (8).



ELLAGIC ACID RESIDUE. GALLIC ACID RESIDUE.

FIGURE V.

Nierenstein observed in 1911 [22] that while ellagic acid itself did not precipitate gelatin, the tetragalloyl derivative did. Further, he observed [6] that

tetragalloyl ellagic acid was a true tannin in the gold-beaters skin test. Thus, many hydrolyzable tannins may be phenolic derivatives of ellagic acid. Thus, Freudenberg and Walpulski[25] have postulated that chestnut wood tannin is the quercitin derivative of monogalloyl ellagic acid. This formula, along with a similar formula for divi-divi, as given by Flinn[8] appears in Figure V. It should be noted, however, that although Nierenstein[6] accepts this formula tentatively, he points out that chestnut wood tannin does not yield the required dimethoxy ellagic acid upon treatment with diazomethane followed by acid hydrolysis.

The attachment of a sugar moiety to these tannins is not clearly established. Their non-tannins are sugar-rich, and it has been postulated that in the plant source the sugar is an integral part of the tannin. However, this has not been proved, and it may be that the tannins of chestnut and divi-divi are not glucosides.

The condensed tannins, or phlobatannins, are much less probably associated with carbohydrates; they are however much more closely related to the plant pigments of the benzopyran type, especially the flavans. Much of the work during the first quarter of this century was concerned with the structure of catechin, a natural flavan found in gambier and cutch.

Fruedenberg *et al.*[26] have converted catechin to cyanidin chloride, whose structure is known. Thus, catechin is 3, 5, 7, 3′ 4′ pentahydroxy flavan. Further, Freudenberg[5] has also identified the six possible stereoisomers. Nierenstein[6] feels that structural isomerism is also probable, with the terminal phenyl group occupying either the 3- or 4- position in the heterocylic ring, instead of the 2-position.

These early papers did not uniquely identify the structure of the particular condensed tannins. However, the formation of phlobaphenes from these tannins suggested some condensation was possible. Bergmann and Pojarlieff[27] postulated that for polymerization, the following structural details are essential:

1. Pyran ring
2. Double bond in the pyran ring
3. Hydroxyl in the pyran ring.

Freudenberg and Maitland[28] showed that 7, 3′ 4′ tri-hydroxy flavan was very sensitive to acid and formed phlobaphene readily. Hence, a pyran ring hydroxy group does not seem to be necessary.

Freudenberg and Maitland[28] have postulated a specific dimerization of quebracho catechin which is shown in Figure VI. It is noted that the dimerization involves the opening of the oxonium ring and the formation of an association dimer which could still further polymerize to give large polymers. This then could be the course of the conversion of the catechins to tannins and phlobaphenes. However, only one natural catechin is known, so that

CONDENSED TANNIN POLYMERIZATION.

ACCORDING TO FREUDENBERG & MAITLAND.

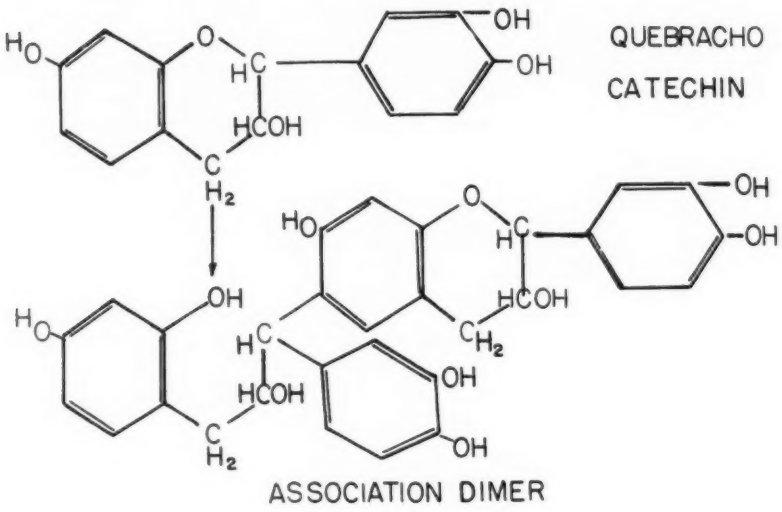


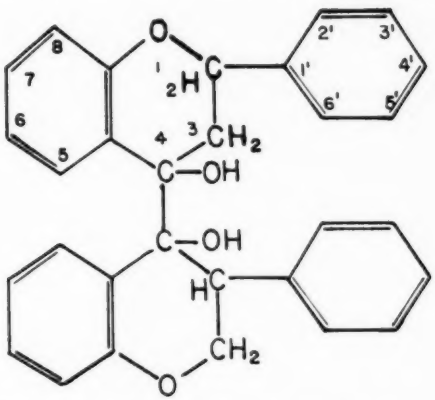
FIGURE VI.

various hydroxy contents of the natural tannins have not been identified with their equivalent polyhydroxyflavan. However, Freudenberg [5] notes that 3, 7, 3′ 4′ tetrahydroxyflavan and 3, 5, 7, 3′ 4′ 5′ hexahydroxy flavan have been synthesized; he further states that these or similar compounds may be the parent substance for quebracho tannin.

We have noted that the structural chemistry of catechin has been in dispute. Further, it was noted that the condensation reaction may require a hydroxyl group in the pyran ring. Generally, this hydroxyl group was thought to be in the 3-position. However, Russell [2 9] investigated the possibility that the phlobatannins might be derivatives of 4-hydroxyl poly hydroxy flavans.

Russell summarized this work in his earlier review [2] to which reference may be made for the original literature citations. Figure VII gives the basic flavopinacol formula which he postulates. The various condensed tannins are thought to be different poly-hydroxylated derivates. Thus, quebracho tannin may be bis (7, 3′, 4′ trihydroxy) flavopinacol; hemlock tannin should be bis (7, 8, 3′, 4′ tetrahydroxy) flavopinacol. Many other tannins are related either to bis (5, 7, 3′, 4′ tetrahydroxy) flavopinacol or bis (5,7, 3′, 4′, 5′ pentahydroxy) flavopinacol. Russell compared these and other synthetic

THE BASIC STRUCTURE OF THE CONDENSED TANNINS. FORMULAE AS SYNTHESIZED BY RUSSELL (2).



HYDROXY-BIS FLAVOPINACOLS.

FIGURE VII.

products to the natural tannins by an extended series of qualitative and quantative organic analyses. Further, he showed that his synthetic products were absorbed quantitatively by hide powder and tan sheepskin skivers. This work has been criticized by Freudenberg [30] and Putman and Gensler [31] from the viewpoint of organic chemistry. We may summarize Russell's work by the statement by Flinn [8]: "Although Russell's preparations appear to approximate closely the natural tannins, there are certain discrepancies (of molecular size and condensation to phlobaphenes) that makes it questionable whether the reactions proceeded along the path he has outlined."

Other specific formulae for condensed tannins have been suggested by Braunschweig [32], a group at the United Shoe Machinery Corporation Laboratory [33] and a group at the South African Leather Industries Research Institute [34]. The structure proposed by Braunschweig includes an inter-molecular secondary valence association of the hydroxy groups of quebracho catechin in an olation-like association. Putman [33b] prefers, for quebracho tannin, a dimeric structure somewhat related to the formulae given by Russell [2], except that the linkage between the two halves is between the phenyl portion of the benzpyran strcutre instead of connecting the pyran portions. However, he states that this preferred structure indicates more than is known at present. Further, he states [33c] that wattle tannin carries the pyran bridge

BLACK WATTLE TANNIN

POSSIBLE STRUCTURE GIVEN BY ROUX

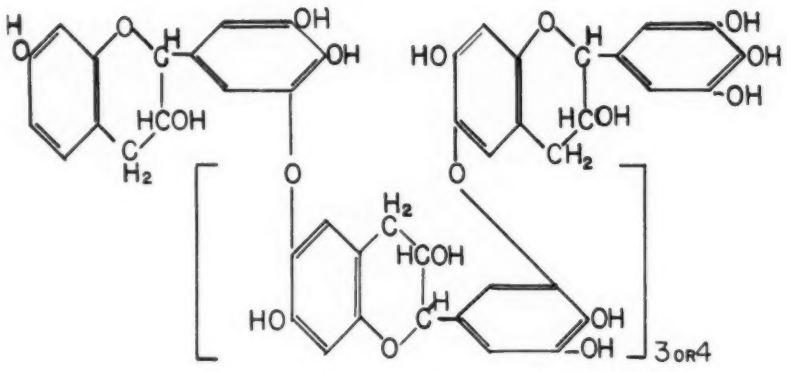


FIGURE VIII.

suggested by Russell[2]. Figure VIII shows a polymeric structure for wattle tannin by Roux[34c].

It is obvious that there is no unanimity with respect to the structure of any of the tannins. It must therefore be asked why this is true. To answer this question we must broaden the traditional approach of the conventional organic chemist to include all of the tools of physical organic chemistry. These data are already beginning to accumulate, and the next section of this paper will review this work.

Physico-Chemical Studies on Vegetable Tanning Extracts

White, Kirby and Knowles[36d] have most cogently stated the scientific philosophy which renders this type of research so important in our knowledge of the structure of the vegetable tannins. They state: "Our investigations were begun with the conviction that elucidation of the chemistry and behavior of any tannin extract requires consideration of all of the extract, not just of part of the initial material isolated by any arbitrary method of purification and considered without reference to the remainder. It was felt too that it was useless attempting to determine the 'chemical formula' of a 'tannin' without first establishing its homogeneity by the strictest means and also demonstrating whether or not it really did constitute the characteristic

tannin of an extract, if indeed such characteristic tannins could be shown to exist. Efforts were concentrated, therefore, on finding out whether quebracho and mimosa tannin extracts have a simple or a complex composition and whether each has its own characteristic tannin. It must be stated very emphatically that both extracts, and most other extracts which have been examined to date [35b], have a complexity of composition far greater than has been previously recognized."

White and his associates [35] have used five primary techniques:

a—Solubility component diagrams.

b—Solvent fractionation.

c—Craig [36] partition of mixtures between immisable solvents.

d—Filter paper chromatography.

e—Column chromatography.

COMPONENTS OF WATTLE TANNIN

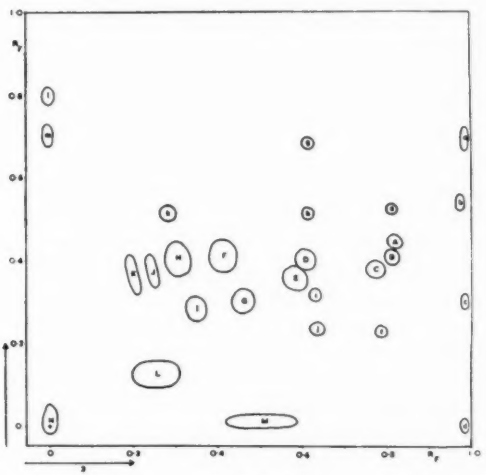


FIG. 9.

Diagram of components of Mimosa tannin extract after chromatography on Whatman No. 2 paper at 20°C with water/*tert*-amyl alcohol/acetic acid followed at right-angles by wet *sec*-butanol. The diagram is a composite of the results with the extract and with fractions obtained by solvent fractionation and by partition between immiscible solvents and shows components made visible by spraying with ammoniacal silver nitrate, or *bis*-diazotised benzidine, or both. No one chromatogram shows all these components and the R_f values are averaged from observation of numerous chromatograms.

THIS FIGURE GIVEN BY WHITE

FIGURE IX.

At least fractional data are available from extracts of tara, tannic acid, valonea, chestnut, myrobalans, cutch, gambier, algarrobo, canaigre, myrtan, quebracho and mimosa. They conclude that mimosa contains at least 37 different substances of which at least one-third are tannins, and that quebracho extract is equally complex. Figure IX has been taken from article by White, Knowles and Kirby[35c] to illustrate the complexity of structure indicated by these approaches. They further note [35d] that some components insoluble as such in water are abnormally soluble in the extract due to mutual solubilization. Some of these insolubles are really not tannins, although they appear as such in the hide powder analysis.

Chromatographic fractionation of the tannins has been reported as far back as the work of Grassman and Lang in 1935[37]. More recently Hillis[38], working in Australia, fractionated commercial extracts of cube gambier, Indian cutch, quebracho, wattle, myrobalans, eucaluptus (Myrtan) and laboratory extracts of mallet and mahogany. His results are in good agreement with those of White. Asquith[39] working on myrobalans extract has found three major fractions, each of which contain at least two components. Clark and Levy[40] employing column chromatography find that aqueous chestnut extracts fractioned under nitrogen contain at least 6 different fractions with different properties.

On the other hand, Putman and Bowles[33g] reject the implications placed on this work by White and his associates[35]. Thus, they state that: "It may be of interest to interpolate at this point certain facts. We have performed in this laboratory a large amount of unpublished experimental work on the purification of vegetable tannins, employing ion-exchange resins, alumina, cellulose, counter-current systems and the like. These have not been reported because they have in large measure, failed to accomplish the desired purification. In our hands counter-current systems have failed because the solubilities of the components present are not independent of each other and thus continually vary during the attempted separations. Studies by infra-red spectrography of the products obtained by such methods have indicated the deceptive nature of many of the separations. It is for such reasons that we have adopted the methods employed. The results given in the present paper indicate a certain degree of success. In the case of quebracho, 67 per cent of the original crude extract consists of the substance(A) having the considerable degree of uniformity revealed here. It is possible that any coloring matters present are of no consequence from the tanning or analytical viewpoints."

We have thus returned after a half century of research to almost the same situation that the present century showed in the first decade. Two different research groups employing similar techniques have arrived at mutually inconsistent interpretations. However, the power of the techniques now being employed on the problem is such that we may soon expect to break this impasse, and arrive at a clear picture of the structural chemistry of the tannins.

The Chemical Properties of the Vegetable Tannins

Because of the indefinite state of our knowledge of the structural chemistry of the vegetable tannins, it is risky to be too specific or positive about their general organic reactions and the mechanism of these reactions. Russell's work [2] has summarized many of the properties of the tannins resulting from their poly-phenolic character.

Shuttleworth and Cunningham [41] have reviewed the theoretical aspects of the mechanism of vegetable tannage. This article contains references to over one hundred articles dealing with the possible reaction mechanisms between phenolic substances and proteins. The review concludes that a hydrogen bonding of the phenolic tannins to the collagen is the most probable mechanism of the tannage reaction.

The phenolic reactivity of the vegetable tannins, especially the catechol tannins, have been used advantageously in several industrial developments. Dalton has shown [11] that tannin formaldehyde resins produce suitable wood adhesives. Monroe [42] has patented the reaction products of quebracho or wattle with benzyl chloride and formaldehyde for wood and leather finish coats. Nico [43] describes the production of plastics from quebracho and hexamethylene tetra amine. Tannin-aldehyde sulfonates have been incorporated into adsorbents [44]. Kremen [45] has utilized this tannin formaldehyde reactivity in his explanation of the increased perspiration stability of formaldehyde retanned vegetable insole leather.

The bisulfiting of quebracho extract to give it a lower degree of cold water insolubles is also a reaction which has been the source of considerable speculation. Bergmann and Pojarlieff [27] postulated that three reactions proceed simultaneously: (1) sulfite ester formation with alcohol groups; (2) addition to keto groups, resulting from phenolic tautomerism, to form hydroxy sulfonic acids; and (3) addition to the aromatic ring to form true sulfonates.

Turley, Somerville and Cronin [46] have developed a method to analyze bisulfited quebracho for the several types of combined sulfur dioxide, and emphasize the role of hydroxy sulfonates in solubilization. Despite this fact, the mechanism of the reaction of bisulfite and quebracho is still in dispute as is witnessed by the debate by White [47] and Balfe [48] in 1948. It seems particularly important to remember the warning of White [47] with respect to the lack of homogeneity of quebracho when considering bisulfite mechanisms.

The various reagents that react with tannins are many. These have been especially developed for the characterization and classification of the tannins. However, in view of the indefinite state of our knowledge of the structural chemistry of the tannins, it seems unnecessary to speculate on the mechanism of these reactions. The reactions just discussed, which are dependent only on the aromatic hydroxyl reactions of the tannins are the significant reactions from the tanning and chemical industry's interests in the tannins.

Summary

Fifty years of research has led to many suggested structural formulae for the vegetable tannins. All of these reflect some or many facets of the chemistry of these materials. Present use of physical-organic method of fractionation of organic systems and study of the structure of purified components have still yielded mutually inconsistent conclusions in the hands of different investigators. However, the techniques now being employed are so powerful for the problem at hand that we may well expect an early solution of the current impasse. We should be on the verge of a correct, detailed knowledge of the structural chemistry of the vegetable tannins.

Bibliography

1. Sequin, Armand, as presented by Lelievre and Pelletier, Annales de Chime **20,** 15-17 (1797).
2. Russell, Alfred, Chemical Reviews **17,** 155 (1935).
3. Procter, H. R., "Leather Industries Laboratory Book," E. and F. N. Spon, Lts., London, England, 1898; Second Edition, 1908.
4. Fischer, Emil, "Untersuchungen uber Depside and Gerbstoffe (1908–1919). Verlag von Julius Springer, Berlin, Germany, 1919.
5. Freudenberg, K., "Tannin, Cellulose, Lignin." Verlag von Julius Springer, Berlin, Germany, 1933.
6. Nierenstein, M., "The Natural Organic Tannins," Sherwood Press, Cleveland, Ohio, 1935; J. and A. Churchill, Ltd., London, England, 1934.
7. Perkin, A. G., and Everest, A. E., "The Natural Organic Colouring Matters." Longmans, Green and Co., London, England, 1918.
8. Flinn, Edwin S., in "Nature of the Chemical Components of Wood," Editor Clarence J. West. Published by the Technical Association of the Pulp and Paper Industry, New York, New York. Page 146. 1948.
9. Freudenberg, K. J., "Die chemie der naturlichen Gerbstoffe." Verlag von Julius Springer, Berlin, Germany, 1920.
10. Fischer, E., and Freudenberg, K., Berichte **45,** 915 (1912).
11. Fischer, E., and Bergman, Max. Berichte **54,** 1760 (1918).
12. Karrer, Salomon and Peyer. Helv. Chim. Acta. **6,** 16 (1923).
13. Nierenstein, M. Annalen **388,** 223 (1912); Pharm. J. **116,** 287 (1926).
14. Nierenstein, M. J. Soc. Chem. Ind. **41,** 29T (1922).
15. Nierenstein, M., Spiers, C. W., and Hadley, A. C., J. Amer. Chem. Soc. **47,** 1726 (1925).
16. Nierenstein, M., Spiers, C. W., and Geake, A., J. Chem. Soc. **119T,** 275-286 (1921).
17. Mitchell, C. A., Analyst **48,** 2 (1923).
18. Russell, Alfred, Tebbens, W. G., and Avery, W. F. J. Amer. Chem. Soc. **65,** 1472 (1943).
19. Russell, Alfred, Tebbens, W. G., and Avery, W. F. J. Amer. Chem. Soc. **64,** 2274 (1942); **65,** 1472 (1943); **66,** 1866 (1944).
20. Schiff, Berichte **12,** 1534 (1879).
21. Perkins, A. G., and Nierenstein, M. J. Chem. Soc. **87,** 1415 (1905).
22. Nierenstein, M., Berichte **44,** 837 (1911).
23. Nierenstein, M., and Potter, J., Biochem J. **39,** 390 (1945).
24. Schmidt, O. T., Heintzeler, M., and Mayer, W. Chem. Ber. **80,** 50 (1947).
25. Freudenberg, K., and Walpulski, H., Ber. **45,** 1695 (1921).
26. Freudenberg, K., Fikentscher, H., Harder, M., Schmidt, O., Ann. **444,** 135 (1925).

27. Bergmann, M., and Pojarlieff, Collegium 239, 244 (1931).
28. Freudenberg, K., and Martland, P. J. Soc. Leather Trades Chem. **18,** 156 (1934).
29. Russell, A., J. Chem. Soc. p218 (1934).
30. Freudenberg, Karimullah and Gustav Steinbrunn. Ann. **518,** 37 (1935).
31. Putman, Robert C., and Gensler, Walter J. J. Am. Lea. Chem. Assoc. **46,** 613 (1935).
32. Braundschweig, Theodore G. J. Amer. Leather Chem. Assoc. **39,** 254 (1944).
33. Putman, Robert C., Gensler, Walter J., and Bowles, Agnes V. J. Am. Lea. Chem. Assoc. (a) **46,** 613 (1951); (b) **47,** 474 (1952); (c) **47,** 478 (1952); (d) **47,** 512 (1952); (e) **47,** 586 (1952); (f) **48,** 124 (1953); (g) **48,** 241 (1953); (h) **48,** 343 (1953).
34. Reviewed by the following:
A. Stephan, A. M., J. Lea. Inds. Research Inst. S. Africa **2,** 127 (1944).
B. Shuttleworth, S. G., J. Am. Lea. Chem. Assoc. **43,** 409 (1948).
C. Roux, D. G., J. Soc. Lea. Trades Chem. **34,** 122 (1950).
D. Roux, D. G., J. Soc. Lea. Trades Chem. **36,** 274 (1952).
35. White, Theodore, Kirby, K. S. and Knowles, E. J. Soc. Lea. Trades Chemists: (a) **33,** 49 (1949); (b) **35,** 338 (1951); (c) **36,** 45 (1952); (d) **36,** 148 (1952).
36. Craig, L. C., J. Biol. Chem. **155,** 519 (1944).
37. Grassman and Lang, Collegium 114 and 401 (1935).
38. Hillis, W. E., J. Soc. Lea. Trades Chemists **35,** 211 (1951).
39. Asquith, R. S. J. Soc. Lea. Trades Chemists **36,** 316 (1952).
40. Clark, L. M., and Levy, W. T. J. Sci. Food Agr. I 213-214 (1950).
41. Dalton, L. K., Austral. J. Appl. Sci., **1054** (1950.
42. Monroe, K. P., U. S. Patent 2,582,500, January 15, 1952.
43. Nico, Paul. Lab. ensayo materiales e invest tecnol., La Plata, Rep. Arg. Ser. 2 No. 38 5 (1950).
44. Bhatnagar, M. S. and Nigam, P. C., J. Appl. Chem. (London) **1** 517 (1951).
45. Kremen, S. S., J. Amer. Lea. Chem. Assoc. **48** 333 (1953).
46. Turley, H. Somerville, I. and Cronin, F. J. Amer. Lea. Chem. Assoc. **36** 329 (1941); **37** 462 (1942).
47. White, Theodore, J. Soc. Trades Chem. **32** 101 (1948).
48. Balfe, M. P., J. Soc. Leather Trades Chem. **32** 25, 214 (1948).

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The Development of Syntans in the United States*

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When plans for this Symposium were being made last summer, it was agreed that one of the outstanding developments in the past fifty years was that of synthetic tanning materials. In September the program committee unanimously invited Dr. Blackadder, as the one best qualified, to present a paper on this subject. He was happy to accept this assignment and in the next few months laid the foundation for this talk by consulting early references in the literature, by contacting by letter some of the authorities in this field, and by drawing on his many years of experience. Unfortunately the work had not been completed when his strength began to fail, and early this

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year he asked your President for a collaborator to finish the paper. I felt honored to accept, in view of twenty-five years of close association with Dr. Blackadder as pupil, colleague and friend.

At the start I should like to take you back forty years to the issue of our Journal which appeared in May, 1913. On page 196 you will find an account of a lecture delivered on March 5 at Ann Arbor, Michigan by a prominent Detroit tanner, Mr. Philip M. C. Armstrong, on "Problems for the Leather Chemist." After a good review of various types of tanning materials, he said, (and I quote) ". . . . This brings up the problem of synthetic tannin. This was formerly considered very important, but has now been found impracticable . . . . In any case it has been shown that tannin alone does not produce a satisfactory tannage, and it is by no means certain that we could employ synthetic tannin for tanning, even if the problem were solved. We have a better chance of success if we turn our attention to tanning by means of metallic salts. The real tannage of the future lies in the development of the present imperfect mineral tannages and the invention of other mineral tannages which will accomplish better results, of course always taking into consideration the cost."

By a curious coincidence, the next paper in the same issue of the Journal, page 208, is by Edmund Stiasny and is entitled, "A Synthetic Tannin." This is a reprint of an article in the Leather World of March 20 of the same year, based on a lecture to the British Section of the International Association of Leather Trades Chemists on March 8, just three days after Mr. Armstrong's prediction about "the real tannage of the future." At this time Dr. Stiasny was on the teaching staff of Leeds University in England and later the same year succeeded Professor Procter in the Chair of Leather Chemistry. However, his work on Neradol had been carried out earlier, and the basic patent applications in Austria and in Germany are dated 1911, those in this country August 20 and December 13, 1912.[1] All these were assigned to the Badische Anilin and Soda Fabrik.

In a private communication to Dr. Blackadder received last November Dr. Stiasny gives some of the background for his invention:

"The observation which led finally to my first syntans was the behavior of formaldehyde towards various vegetable tanning materials. This study uncovered the fact that phenolic non-tans in the filtrate from treating catechol tans with hide powder are completely precipitated by formaldehyde while pyrogallol non-tans are not precipitated. Surprisingly, however, these pyrogallol non-tans after reaction with formaldehyde gave a precipitate with gelatin, hence non-tans had been changed into tans! This led to the investigation of various phenols and phenol derivatives . . . "

In the first announcement on March 8, 1913, Stiasny drew a distinction between synthetic tannins – i. e., those having the same constitution as the natural tannins but made synthetically (e. g., synthetic and natural indigo)—

and the artificial tannins, i. e., those showing only analogies and resemblances in constitution and behavior, (e. g., aniline dyes as a substitute for natural dyestuffs). The first approach was ruled out because of price considerations, the second taken up in an endeavor to make products similar to the tannins which would convert hide into leather. "One solution was achieved by the action of formaldehyde on phenolic bodies under such conditions that only water soluble products are obtained." The example quoted from the Austrian Patent No. 58405 reacted cresylic acid with an equivalent amount of sulfuric acid at 100–120°C, cooled and added slowly half an equivalent of formaldehyde, then alkali to neutralize the free mineral acid, forming Neradol. The possibility of first condensing the phenol with formaldehyde to form a Novolak then sulfonating was also disclosed in the basic patent. The designation "syntan" was coined by Dr. Stiasny and applied at this time.

This discovery received wide publicity and in our Journal for 1913 a number of papers testify to the interest shown in this new approach to tanning. Those by Eitner [2] and Grasser [3] were favorable, but Moeller [4] objected to calling it a synthetic tannin. The practical applications were reported for the Badische by Durdorf [5] who stressed that the first role of Neradol was in the tannage of light leathers, but that greater benefits could be secured by using it along with vegetable tannins, as a pretannage in handlers (up to 5 per cent) and as a bleach for the tanned hides. In the Journal for 1914 there is an account by Stiasny [6] of the method of use by itself on bated and pickled skin, emphasizing its value in conjunction with vegetable tannins, in retannage of East India kips, and its possibilities along with chrome, alum, and formaldehyde tannage. He claimed that nearly white leather could be obtained by suspending well chromed skins in a 5 per cent solution of Neradol D. Finally he stated, "... the results justify the conclusion that the problem of synthetic organic tannins of technical importance is now solved."

In criticism, Nierenstein [7] stated in a review on Syntans, "Professor Stiasny has utilized most ingeniously in their preparation an old discovery of Baeyer (1870) who noticed that pyrogallol forms a tannin-like substance when condensed with formaldehyde." There were others around that period who had experimented with condensation reactions resembling Stiasny's, but that does not detract from the unique results which he demonstrated in preparing syntans which could be used to make leather on a practical tannery scale.

The product Neradol was quickly put on the market in this country, first being sold by Dr. Otto Kress who recently retired as Director of the Paper Institute at Appleton, Wisconsin. In March he wrote me his impressions:

"Neradol was not put out as a tanning agent to be used alone but from my work it was a pretan, the depth of penetration being measured on a cut edge by means of a dye that was one of the Indulines. The main talking point of the product was a saving in time, for after the Neradol treatment we

followed with much stronger regular tanning liquors and the grain was not drawn or raised . . . With the entry of the United States into the war importation of the product ceased but we sold all the shipments that had arrived prior to that time . . . ."

World War I caused many more important upsets than the development of syntans, but one result was that the Badische Anilin Soda Fabrik lost its monopoly on products of Neradol type. In Britain a number of products similar to Neradol D came on the market, made under government license, under the names of Paradol, Cresyntan, Synthetic Tannin and Syntan [8]. In this country several of the basic syntan patents [1] were issued in 1917 and many attempts were made to imitate the German products. Incidentally, by this time the initial condensation of phenolic products with formaldehyde had been extended to cover the use of higher aldehydes, [9] and more importantly the utilization of aromatic compounds free from hydroxyl groups, particularly starting with the cheaper naphthalene in place of phenol as raw material. [10]

We are indebted to Mr. Clyde Carter of the Robeson Process Company for information about one of our charter members, John Yocum, who took up the manufacture of syntans here on the basis of information available at that time, probably using German patents licensed by the Alien Property Custodian. He soon developed what was called *Liberty Extract*, a formaldehyde condensate of naphthalene sulfonic acid, which showed 35 per cent of "Tannin" absorbed by hide powder and contained 18-20 per cent of free mineral acid, as indicated by the Procter-Searle method. The ash was low, and when added in yard tannage to the third liquor from the tail a decided increase in plumping was obtained. This method of use, applied in moderation, did not cause damage to the hides and was safer than the addition of sulfuric acid commonly used in the so-called "acid tannage", in which limed hides were swelled in dilute sulfuric acid then tanned using either oak bark or hemlock bark, depending on the geographical location of the tannery. An early association of E. C. Klipstein and John Yocum was broken up in 1918 and the former continued to manufacture Liberty Extract while the Yocum Laboratories made a similar product called *Synex*.

Other raw materials were considered as starting points for syntans. Crude cresylic acids were tried but proved unsatisfactory because of variations in composition. A crude salicylic acid available as a by-product in the manufacture of saccharin was successfully utilized by Rohm and Haas Company to make *Cresotan*. Some other products put on the market caused trouble due to the presence of excessive or dangerous acid—a feature which was accentuated at the end of the war when a bad slump in the price of sole leather occurred. Large inventories had to be held over and in some cases bad acid deterioration occurred—syntans as a whole were blamed and fell into disrepute. Mr. Carter believes, however, that these difficulties did not

occur with most syntans when used properly but may have arisen when an excessive amount was added in the head liquor or more probably were caused by too heavy loading with organic specialties.

About this time more information became available on syntans. A book on "Synthetische Gerbstoffe" by G. Grasser was published in Germany in 1920 and translated into English by F. G. A. Enna in 1922. Some important papers appeared in our Journal, among them:

(1) By H. Bamberger on "The Artificial Tannins"[11], referring to early work by Schiff in 1875 on depsides of phenolsulfonic acid and going on to extend condensation reactions of the Stiasny type;

(2) By G. Grasser on "The Synthesis of Tanning Substances",[12] reviewing a good deal of the same ground and concluding, ". . . All mono- and polyhydric phenols can be converted into true tanning agents by condensation with dehydrating substances before or after converting into soluble sulfonic acids. The end effect remains the same whether the condensation takes place first and then converting this insoluble product into a water soluble product by sulfonation, or vice versa, by condensing the sulfonic acid . . . ";

(3) By Rohm and Haas Company on "Synthetic Tans",[13] dividing these materials into two general classes: I. Those which in concentrated form (20° Baumé) and at ordinary temperatures do not attack hide substance (*Ordoval*) and, II. Those which do (Neradol D). "The latter have been largely displaced by the former." In practical application these were recommended particularly for use in conjunction with vegetable tannins, and it is specifically stated that they showed no marked advantage for retanning or mordanting chrome leather.

The potential value of syntans to the national economy was first considered in this same period, the situation being reviewed in a classic paper by Edward Wolesensky.[14] In 1924 a survey by the U. S. Department of Commerce stated that 40 per cent of the vegetable tanning materials consumed in the United States in 1922 were imported. In addition it was recognized that the inroads of the chestnut blight were reducing the supply of our principal domestic tannin. Further, it was pointed out that 99 per cent of our chrome ore was imported at that time. These facts led to a decision to investigate other sources of tanning materials for supplementing and replacing the vegetable tannins and chromium. This work was carried out at the Bureau of Standards, and the results were reported in a series of papers which appeared in 1925 and 1926. In the most important, Wolesensky prepared representative syntans of various types according to the information available at that time and evaluated them by tanning tests. The conclusions reached differentiated clearly between (a) products derived from hydrocarbons containing no phenolic groups, (b) those based on aromatic compounds with one phenolic hydroxyl

made either by sulfonating first or by condensing first, and (c) those based on polyhydric phenols without sulfonic groups. Class (a) showed only inferior tanning properties. Class (b) made by sulfonating first possessed true tanning properties, giving soft, pliable light weight leathers but lacking necessary filling qualities for heavy leathers. Those made by condensing first were also good tanning agents and had better filling properties. Class (c) possessed filling properties to a greater degree than any of the sulfonated products and produced very good leather.

These results laid a good foundation for more extensive development of syntans from the angle of their national importance. However, lack of foresight on the part of those responsible for allocation of funds made it necessary to stop this work at the Bureau of Standards. Mr. E. L. Wallace informed me recently that Wolesensky was let out in this economy move, and was never able to proceed further with this problem on which he made such a promising start.

One theme which keeps recurring all through the story of the commercial development of syntans is cost, cost, cost. For example, leather made with the resorcinol-formaldehyde condensates prepared by Wolesensky had many of the characteristics of vegetable tanned leather, but the cost then was prohibitive. The industrial utilization of syntans was determined therefore by finding how to apply them to economic advantage. The trend in the country of origin, Germany, was quite different to that in this country—there the emphasis was put on making a large number of specialties blended for specific purposes, while here a relatively few selected types of syntans were offered to the tanners with general recommendations for the best methods of application. Another important feature of their development in this country was their successful promotion on chrome leather, a field in which the senior author made a major contribution to the industry. This resulted in a large outlet for syntans in the preparation of bleached chrome leather, still the customary method of making utility whites. The use of neutral syntans such as *Tamol* in conjunction with Acid or Direct dyes to secure level coloring on pastel and light shades, and for mordanting Basic dyes to produce full colors, dates also from this period.

Around 1930, some of the better syntans developed abroad became available in this country, and were used to produce a small volume of premium white leather on expensive skins such as reptiles. *Irgatan* was one of the first of these, and some grades of *Tanigan* were also effective. The increased cost of such raw materials as benzidine or phenolsulfone was recovered in the higher selling price of these specialty leathers. Some domestic syntans in this price class made their appearance, and featured good stability to sunlight and to oxidation. These were also utilized to some extent in bleaching chrome leather, where the additional fullness was frequently of more importance than the improved light stability. The latter is generally taken care of by the use of

pigment after fatliquoring and the subsequent application of a protective finish.

In the years preceding World War II, the political situation in Germany and extreme emphasis on national self-sufficiency intensified their interest in synthetic tanning materials. Many papers by such well known authors as Schütte, Otto, Stather, Löchner, Herfeld, Loewe and Felzmann were published and increased greatly the fund of knowledge in this field. Under the type of economy then prevailing the cost factor was minimized or eliminated and several products were developed which were claimed to be complete replacements for vegetable tannins. However, it may be significant that reports by teams of Allied investigators at the end of the war indicated that leather prepared using these materials alone was not utilized in making heavy leather for the German Army.

In this country a number of chemical manufacturers were active in the syntan field in the later nineteen thirties, each having a range of products with familiar trade names:

Tanak	(American Cyanamid Company)
Adcotan	(American Dyewood Company)
Arkotan	(Arkansas Company)
Gycotan, *Sellatan*	(Geigy Company)
Mertanol	(Monsanto Chemical Company)
Naccotan	(National Aniline & Chemical Company)
Leukanol, *Tamol*	(Rohm & Haas Company)
Tanasol, *Synektan*	(Jacques Wolf & Company)

All were interested in the development of new products, and at the threat of war many directed part of their research program towards the preparation of syntans which could replace or at least supplement the available supply of vegetable tannins. In some instances this involved picking up the work where Wolesensky had left off fifteen years previously. A cooperative project between the Monsanto Chemical Company and the Tanners' Council Research Laboratory seemed to offer a promising solution. The product *Exan* was put on the market, but apparently did not prove adequate under practical tannery conditions. In the meantime, Dr. Turley worked out in the Rohm & Haas Laboratories a material designated *Orotan TV* which looked promising in small tannery trials and subsequently proved to be a complete tanning material in itself. This achievement was reported at a sectional meeting of our Association in New York City in 1944 in a paper entitled,

"A New Synthetic Tan That Can Replace Vegetable Tans."[15] The results indicated that this product could be handled in the same way as a vegetable extract and would give leather of good quality with a degree of tannage comparable to that found with the best vegetable tannins. Some years later large scale tannery tests were run and reported on by Marshall and Turley in 1949 in a paper entitled, "Tanning Sole Leather With a Synthetic Tan."[16] These demonstrated that this product could be used alone to prepare sole leather which met all government specifications. As in the case of the much publicized rubber field the synthetic product was more expensive than the natural product but likewise turned out to have some distinctive advantages which have extended its use in applications where the increased cost is more than justified by better performance.

The period since the war has seen the appearance on the U. S. market of other syntans such as:

Chemtan	(Chemtan Company)
Leather Product X59A	(American Cyanamid Company)
Microtan	(Reilly-Whiteman-Walton Company)
Nopco 1187*X*	(Nopco Chemical Company)
Trutan	(A. J. & J. O. Pilar)

Some of these are modifications of earlier types mentioned, while others were formulated on the basis of information on the composition of German syntans brought back by teams of Allied investigators.[17] These include tan-assists for use along with vegetable tannins, better quality products for making white leather, and replacements for vegetable tannins.

A related development not strictly in the syntan field has been the recent trend towards the impregnation of skins with aqueous solutions of organic co-polymers, with subsequent fixation in the hide fibre by appropriate means. These materials include:

G-942	based on styrene-maleic anhydride (E. I. du Pont de Nemours & Co., Inc.)
Tanak MRX	based on melamine-formaldehyde (American Cyanamid Company)
*Chemtan R*44	based on dicyandiamide-formaldehyde (Chemtan Company).
Leotan A	based on methyl vinyl ether-maleic anhydride (General Dyestuff Corporation)

In this way additional filling can be secured even though the materials themselves have no pronounced tanning properties. The ultimate merit of products of this type has still to be determined. Some of these methods are listed in P. C. Chen's book on "Syntans and Newer Methods of Tanning" published in 1950.

Summary

In conclusion, the story of syntans has been traced back forty years to its practical beginning with Neradol. The influence of World War I is obvious in the subsequent development, which followed entirely different lines in this country to that in the country of origin. The initial use of syntans in conjunction with vegetable tans was supplemented here to an important extent by their use on chrome leather, a possibility mentioned by Stiasny but not exploited earlier. The conditions created by World War II emphasized the need for a syntan which could supplement the dwindling supplies of vegetable tannins.

Perhaps Stiasny was a little premature in claiming that "the problem of synthetic organic tannins of technical importance is now solved," since the first commercial product gave soft, pliable light weight leather admittedly lacking in filling qualities. However, there are now products available in this country comparable to the best vegetable tannins in conferring fullness and high degree of tannage. The ultimate aim of a syntan with a tan unit cost as low as that of the cheapest vegetable tannins still lies ahead.

References

1. Austrian Pat. 58,405; German Pat. 262,558; U. S. Pats. 1,237,405; 1,232,620.
2. Eitner, *J.A.L.C.A.* **8,** 361 (1913).
3. Grasser, *J.A.L.C.A.* **8,** 404 (1913).
4. Moeller, *J.A.L.C.A.* **8,** 479 (1913).
5. Durdorf, *J.A.L.C.A.* **8,** 394 (1913).
6. Stiasny, *J.A.L.C.A.* **9,** 230 (1914).
7. Nierenstein, *J.A.L.C.A.* **11,** 227 (1916).
8. Wood, *J.A.L.C.A.* **12,** 487 (1917).
9. U. S. Patent 1,254,364.
10. U. S. Patents 1,191,480; 1,216,612; 1,222,033; 1,278,229; 1,289,280.
11. Bamberger, *J.A.L.C.A.* **14,** 639 (1919).
12. Grasser, *J.A.L.C.A.* **16,** 20 (1921).
13. Rohm and Haas Company, *J.A.L.C.A.* **19,** 111 (1924).
14. Wolesensky, Technologic Papers of the Bureau of Standards # 302.
15. Turley, *J.A.L.C.A.* **40,** 58 (1945).
16. Marshall and Turley, *J.A.L.C.A.* **44,** 870 (1949).
17. Schultz and Schubert, "An Investigation of the German Leather Industry". A.P.O. 757. Appendix 1, 2 and 3.
    Johnson, "German Synthetic Tanning Agents" Leather Series—Report # 2 Office of the Quartermaster General.

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Dyes for Leather†

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In connection with the Golden Jubilee celebration I want to tell you a little of the progress made in dyes, and in dyeing of leather during the last fifty years.

I would like to review with you the various chemical classes in which leather dyes fall, the history of these classes and the development of their application to leather.

Classification

Dyes may be classified in several ways. While the manufacturer will arrange them by chemical type such as azo, anthraquinone, triphenyl methane, etc., the consumer is interested in uses regardless of constitution.

The following classification includes the types of most interest to the leather industry:

1. *Basic Dyes*

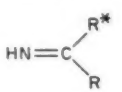
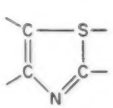
This term does not refer to an alkaline reaction but to the fact that these dyes contain primary, secondary, or tertiary amines which form salts with acid. Usually the water-soluble dyes are hydrochlorides, sulfates, or oxalates.

They produce bright, strong shades of relatively poor light fastness.

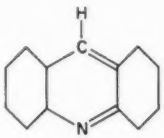
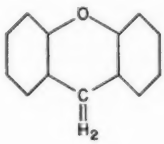
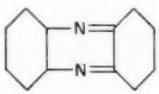
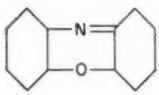
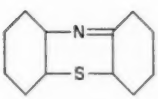
Formerly applied to cotton with a tannin mordant, they now find little use on textiles. In addition to their use on leather, they are important in coloring paper, carbon paper and typewriter ribbons and for conversion to pigments.

†Presented at the Golden Jubilee Meeting of the A.L.C.A. in Cincinnati, Ohio, June 9, 1953.

Basic dyes commonly used on leather include the following types:

	Chemical Class	*Color Nucleus*	*Examples*
A	Ketonimine		Auramine
B	Thiazole		Thioflavine

*R = aromatic radical

C	Acridine		Phosphine Basic Orange
D	Azo		Chrysoidine Basic Brown
E	Xanthene		Rhodamine
F	Triphenyl Methane		Fuchsine Crystal and Methyl Violet Victoria Blue Victoria Green
G	Azine		Safranine
H	Oxazine		Meldola's Blue
I	Thiazine		Methylene Blue

Basic dyes are important on leather to obtain full shades and brilliance. They will dye vegetable-tanned leathers without a mordant but chrome-tanned leather must be mordanted with syntans or acid dyes to be substantive to basic colors.

II. *Acid Dyes*

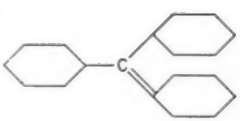
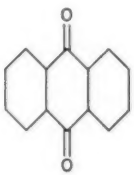
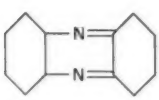
Here again this term does not refer to the pH of the dyes but rather to the fact that they are normally used to dye wool in an acid bath. Most acid dyes are sodium salts of sulfonic acids. Some of the oldest are sulfonates of

basic dyes. Sulfonated anthraquinone types also represent an important class.

These types are used on animal fibers and are particularly important on leather but have no affinity for cellulose. They are retained on paper by the use of rosin size and alum. Heavy metal salts of acid dyes are used as insoluble pigments.

The brightness and light fastness of these colors vary widely, these properties depending on the color nucleus.

Acid dyes commonly used on leather include the following types:

	Chemical Class	*Color Nucleus*	*Examples*
A	Azo	—N=N—	Tartrazine Light Yellow 2G Orange II Orange G Leather Browns Crocein Scarlet Milling Red Scarlet 2R Blue Black SX Resorcin Browns
B	Triphenylmethane		Violet 4 BL Brilliant Milling Blue Brilliant Blue A Brilliant Blue V Green NV
C	Anthraquinone		Anthraquinone Blues Anthraquinone Greens
D	Azine		Nigrosine

On leather, acid dyes penetrate well and in general produce level dyeings. They are used extensively on chrome tannages.

III. *Direct Dyes*

These dyes derive their name from the fact that they will dye cotton directly without the use of mordants. Chemically they are similar to acid dyes in that they are generally sodium salts of color sulfonic acids. Unlike acid dyes they form colloidal systems which are substantive to cotton. In addition to cotton they are used on rayon, cellophane, paper, and leather.

Brightness of shade and fastness to light vary with chemical constitution.

Practically all direct dyes belong to the Azo class. Included are the following of interest on leather:

Fast Yellow NNL
Stilbene Yellow
Brown N3G
Catechu
Bordeaux B
Scarlet 8BS
Blue AX
Blue BB
Sky Blue
Green GX
Black E

Direct dyes exhibit but little substantivity for vegetable tanned leaathers. When used on chrome-tanned stock, they tend to dye the surface only unless alkali is used to promote penetration.

IV. *Mordant Acid Dyes*

Acid azo dyes having a hydroxyl or carboxyl group ortho to the azo group or acid dyes having hydroxyl and carboxyl groups ortho to each other are capable of forming metallic complexes. Chromium salts are the most common source of metal and are used to aftertreat the dyeing. The resulting color is usually duller in shade but faster to light and wet treatments.

These dyes are rarely afterchromed on leather but comprise an important class when used like straight acid dyes. They are characterized by level dyeing, penetrated shades which in general have good wash fastness. They are of particular interest on glove and garment leathers.

The following are examples of this class:

Chrome Yellow 3RN
Chromate Brown EBN
Chrome Brown RH Conc.
Chrome Brown RN Conc.
Chrome Red A4B
Chrome Black F conc. 125%.
Chrome Blue Black RM Conc.

V. *Premetallized Acid Dyes*

The premetallized acid dyes may be considered chrome colors in which the metal complex has already been formed. They are sufficiently soluble to enable application to animal fibers and leather by methods analagous to those used for acid dyes. The exact chemical structure of these is not definitely established.

This type is sold under trade-marks of "Chromacyl," "Neolan," "Palatine Fast," "Chromolan," "Vitrolan," and "Gycolan."

VI. *Developed Dyes*

Direct colors containing a free amino group can be developed on leather by diazotizing the amino group and coupling to aromatic developers containing hydroxyl or amino groups.

This process improves the wash fastness of the original direct dye.

In the case of leather this process is usually used for black shades in which the developer is meta-toluylene diamine. In the case of suede leather particularly, a full black of uniform penetration is obtained.

VI. *Spirit Soluble Dyes*

Basic and many acid dyes are soluble in alcohol but are also soluble in water. In order to reduce water bleed of dyes for use in spirit stains on leather two types of dyes are available.

A. Basic dyes mechanically mixed with tannic acid. This mixture is soluble in alcohol. When water is applied, the tannate of the basic dye which is insoluble in water is formed.
B. Acid dyes converted from sodium to guanidine or similar salts. These salts of acid (and some direct) dyes are soluble in alcohol but insoluble in water.

History

For centuries all dyeing was done with natural dyes of animal, vegetable or mineral origin.

Natural indigo, woad, saffron and madder, all of vegetable origin were used by the ancients to produce blue, yellow and red colors. Small insects furnished cochineal, while shellfish were the source of the very expensive Tyrian purple. A price fixing edict of AD 301 set the price of wool at about $1.50 per lb. Heavily dyed with Tyrian purple the price was $350 per lb. It is no wonder it was used only by royalty.

When trade with India was inaugurated, cutch and gambier obtained from certain trees were used for brown shades. Later from America fustic and logwood became important dyes.

Many of these products will still be familiar to those of you in the leather trade.

In recent years natural dyes have been almost completely replaced by synthetic dyes.

Indigo, one of the oldest natural dyes, was the starting material for the first synthetic dyes. In 1771 Woulfe obtained a yellow dye by the action of strong nitric acid on Indigo. This was picric acid.

The synthetic organic dye industry actually dates from Perkin's discovery of mauve in 1856. Perkin, trying to produce quinine by the oxidation of aniline, found a tarry mass which dissolved in alcohol to give a purple solution. This material could be used to dye wool and cotton (with the aid of tannin mordant). It was one of a group of basic dyes and represented the first synthesis of a dye from essentially uncolored starting materials. Basic dyes, as stated previously, have important applications to leather.

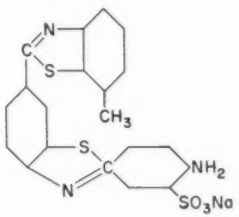
In 1858 the diazo reaction was discovered, thus opening a new field of dye chemistry. Basic Brown has been produced commercially since 1863 and is still an important leather color. Many other azo dyes of the acid, basic and direct class are used on leather today.

The next important discovery was the synthesis of alizarine in 1868. This dye was combined with a metal on the fiber to form the insoluble Turkey Red lake of superior light fastness.

In 1880 an insoluble azo dye was formed on the fiber with the discovery of Para Red. The fiber was impregnated with B-naphthol and then treated with diazo p-nitro aniline, thus producing an insoluble pigment in the fibers. It was the forerunner of the present azoic dyes.

In 1884 Congo Red, the first of the soluble azo direct cotton colors was discovered.

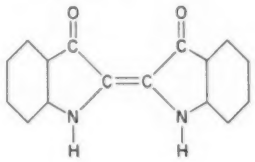
The discovery of Primuline in 1887 led to a new method of dyeing. This compound



has affinity for cotton. After application to the fiber the amino group is diazotized and coupled to B-naphthol. This process is related to the application of developed colors on leather.

Sulfur dyes were developed in 1893. They are soluble in sodium sulfide solutions from which they are applied with subsequent insolubilization on the fiber.

It was in 1894 that synthetic Indigo appeared on the market. It is insoluble in water and has the following formula:



When reduced chemically in alkaline solution, a soluble "leuco" is produced, the carbonyl group becoming C-O-Na. This "leuco" is padded on the fiber (it has little affinity) and is then oxidized back to the insoluble form.

In 1901 anthraquinone vat dyes were discovered. They are applied from a reducing medium as is indigo but the "leuco" form unlike that of indigo is substantive to cotton. It is this class of dyes that has given the modern light and wash-resistant "vat" dyes now considered essential for quality dyeings on cotton.

In 1922 stable sulfuric esters of "leuco" vat dyes were developed. This permitted simpler but more expensive application of the vat dyes. They can be applied without the use of strong alkalies by direct dyeing with subsequent oxidation on the fiber.

With the introduction of cellulose acetate fibers in the early 1920's, dyes for this fiber were developed. Since cellulose acetate dyes by solid solution, the colors used are water insoluble anthraquinone or azo derivatives which are applied from a dispersion of the dye in water.

About 1924 the chromiferous dyes were marketed. They are azo dyes containing chromium in the molecule, making addition of chrome to the dyebath unnecessary.

In the early 1930's phthalocyanines were developed. It was stated that they contained the first new chromophore group in 50 years. These materials are essentially blue and green pigments although water and alcohol soluble types of the blue are available.

It will be seen from this history that most of the types now used on leather were available 50 years ago. The literature of that period indicates that synthetic dyes were rapidly supplementing and replacing the natural extracts. Brighter and more varied shades were available and a uniformity of shade became possible which could not be had with extracts of variable color.

However, many changes in the dyeing of leather have taken place during this period. The quality of the dyes has improved greatly over the years. Many improvements in removing impurities from intermediates and dyes have been effected. Solubility and stability of dye solutions have been improved.

Many new dyes have been synthesized especially for use on leather. Dustless types have been made to aid the handling of dyes in a tannery.

Not only have the quality and uniformity of the dyes improved but many refinements in application methods and equipment have been made. Tray and paddle dyeing methods have been largely replaced by drum methods. The drums have been improved to permit proper stock-to-liquor ratio and to produce more efficient agitation with better handling of the stock.

Technical staffs of suppliers have built up a scientific background so that the best available dye and method can be recommended for any given condition.

A great deal of progress has been made but obviously much remains to be done. The present trend indicates that it will be necessary to improve light, wash and crock fastness properties. Unfortunately the use of the present syntans, filling materials and vegetable extracts seriously limits the affinity of dyes other than basic colors which are fugitive to light.

Leather, as it is now tanned, will not tolerate the strongly alkaline conditions necessary for the application of vat dyes which would produce excellent fastness results.

The application of dyes to leather should be improved. In many cases such a low volume of water is used that the dye is not completely dissolved. Dyes are frequently forced on to leather by the addition of acid instead of allowing normal exhaustion to take place. Such forcing results in plating of precipitated dye on the surface of the leather.

There is a need for the development of basic dyes having better wash and light fastness and acid dyes having affinity for syntans and extracts.

Finally since leather is a costly material, it should be prepared with the utmost color appeal and utility. Appearance is an important factor in sales. Therefore stringent price limitations of dyeing and careless selection and application of dyes should be avoided.

Received June 12, 1953.

ABSTRACTS

Spruce-Bark Tannin. III. Change of the Alcohol-Precipitation Number on Damp Storage of Spruce Bark. By A. Haglund. *Das Leder* **4**, 55 (1953) (*see This Jour.* **47**, 446). Spruce bark was analyzed fresh and after storage under humid conditions for from 1 to 3 weeks. The following analytical results were obtained:

	Fresh bark	Bark stored damp for 1 week	2 weeks	3 weeks
Alcohol precipitation number	25	46	48	52
Purity	50	66	69	70
Phlobaphene number	1.07	1.13	1.17	1.38

A fractional extraction was made of bark stored damp for 3 weeks with the following results:

	Number of the extract			
	1	2	3-5	6-13
Fresh bark				
Tannin, grams (g)	86.0	71.3	214.5	202.5
Nontannin, g.	98.0	62.7	108.0	180.5
Insolubles, g.	0.6	0.0	4.4	13.0
Alcohol precip. no.	16.4	15.2	26.1	60.1
Viscosity, CP at 15% TS.	2.1	2.4	5.5	9.7
Stored bark				
Tannin, g.	87.5	68.3	161.4	236.0
Nontannin, g.	47.5	41.2	90.9	211.9
Insolubles, g.	14.0	12.5	5.9	15.8
Alcohol precip. no.	37.5	37.8	42.2	55.4
Viscosity, CP	19.2	11.5	9.2	9.0

Finally, 100 gram portions of bark, chopped to 0.5-1 cm. lengths, were stored under the following oxidizing-condensing conditions:

I. analyzed at once.

Four portions were treated with 50 per cent of their weight of water then stored 7 days as follows:

II. stored in an open flask.

III. stored under nitrogen.

IV. treated with 1 per cent $NaHSO_3$ then stored open.

V. heated 2 hours in a boiling water bath then stored open.

After storage the bark was dried, ground, and analyzed with the following results:

	I	II	III	IV	V
Tannin, % of dry bark	23.7	25.5	23.7	24.3	24.7
Nontannin, % of dry bark	13.2	8.3	13.6	15.5	15.9
Insolubles, % of dry bark	1.7	4.6	3.0	2.2	3.9
Total solubles, % of dry bark	38.6	38.4	40.3	42.0	44.5
Alcohol prec. no.	31	43	32	28	38
Total solubles x alc. prec. no.	12	16.5	12.9	11.8	17

The results show that there is an increase in a short time in the alcohol insoluble portion of the water extract of spruce bark stored damp with access to air. On fractional extraction of a damp stored bark there is a large increase in the alcohol insoluble tannin (Fraction I) and in viscosity of the first fraction. The additional tannin in fraction I is therefore characterized by a very high viscosity. On further extraction the viscosity decreases. This anomalous viscosity is explained by the fact that the tannin at the surface of the bark undergoes an oxidative-condensation under the influence of oxygen of the air, moisture and

bark enzymes. Tannin at the surface of either fresh or stored bark dissolves first on fractional extraction. Insofar as the nontannins have the same basic structure as the tannin, they change to tannin on oxidative condensation. On the other hand the tannin condenses to an alcohol insoluble form (Fraction I) or to water insoluble phlobaphenes. It is improbable that the alcohol insoluble fraction condenses further to phlobaphenes. Apparently there are different, parallel, condensation processes in which the formation of Fraction I strongly predominates. I. D. C.

Tannin of Seaweeds. By T. Katayama. *J. Chem. Soc. Japan* **54,** 603 (1951). Through *Chem. Abst.* **47,** 7245 (1953). Tannin was determined in the seaweeds *Ecklonia bicyclis*, *E. cava*, and *Phyllospadix oxyphyllus* collected on the coast of Wakamatsu, Tukuoka Prefecture. The maximum content at maturity was about 14 per cent.

Structure of Collagen. II. Stress-Strain Behavior of Thermally Contracted Collagen. By N. M. Wiederhorn and G. V. Reardon. *J. Polymer Sci.* **9,** 315 (1952). Through *Chem. Abst.* **47,** 7245 (1953). Kangaroo tail tendons were soaked 15 hours in 15% NaCl solution to remove globular proteins, extracted with Et_2O, shrunk by being placed in boiling H_2O for 2-3 minutes, plunged into cold H_2O, and air dried at room temperature. Before stress-strain analysis tendons were soaked over night at 40° in the medium in which the test was to be run, then 4 hours in the same medium at the test temperature. The tendon was mounted between two clamps, the upper of which was attached to a metal rod suspended on a cantilever beam on which was mounted an sR4 strain gauge, and the lower of which was attached to a rod running through the bottom of the thermostat bearing a mark for cathetometric determination of length change. Measurements were made in H_2O, $HCHNH_2$, and M LiCl in 1:1 H_2O-EtOH, and the molecular weight (Mc) of the chains between points of cross linking was calculated from $f = (RT\rho v_2{}^{1}/_{3}/Mc)(a - {}^{1}/a^{2})$, in which f is the retraction force per unit area, ρ is density of the dry tendon, v_2 is volume fraction of the tendon in the swollen structure being stretched, a is extension, and Mc is molecular weight of chains between points of cross linking; Mc is approximately 55,000.

Lubrication of Buret Stopcocks. By W. Kirsten. *Anal. Chem.* **25,** 1137 (1953). The buret is thoroughly cleaned and the ground glass surfaces of the stopcock are treated with Dri-film (General Electric Co.), Desicote (Beckman Instrument Co.), or a similar silicone reagent. The stopcock is then lubricated with an ordinary organic lubricant. As the stopcock has thus obtained an organic, nonwetting surface which sticks well to the lubricant, the water cannot creep in and buret stopcocks become perfectly tight.

Rapid Modified Procedure for Determination of Kjeldahl Nithogen. By C. H. Perrin. *Anal. Chem.* **25,** 968 (1953). By adhering to the modifications of the Kjeldahl-Wilfarth-Gunning method for nitrogen, the author claims a pronounced reduction in the digestion time. Procedure is as follows. Place a 0.5- or 1.0- gram sample in a dry 500-ml. Kjeldahl digestion flask and add approximately six smooth boiling silica granules, 1.3 to 1.5 grams of mercuric oxide, and 12 ± 0.5 grams of potassium sulfate. (Add no filter paper or other matter.) Swirl flask to mix, add 15 ± 0.5 ml. of concentrated sulfuric acid, and mix again. Digest for 5 minutes (or until frothing ceases) at low heat, then boil at "full heat" until digestion is complete. (By full heat is meant a heating intensity

sufficient to bring to a rolling boil 250 ml. of water in a 500-ml. Kjeldahl flask in from 4 to 5 minutes. This is called the boil test.) Heating conditions are correct for most samples if the following schedule is obtained:

Low heat	5 minutes
Full heat	8 to 12 minutes
Total digestion time	13 to 20 minutes

The total time required for complete clearing should be from 10 to 14 minutes. Avoid intense heating of flask above level of liquid. When digestion is complete, cool and promptly add about 200 ml. of cold water. Swirl if necessary to dissolve the cake and add in quick succession (and in the following order) approximately 25 grams of sodium hydroxide pellets, 5 grams of sodium thiosulfate pentahydrate, and 0.5 grams of 20-mesh zinc. Connect to the Kjeldahl distillation apparatus and receive ammonia in about 75 ml. of the boric acid solution. Titrate with standard acid using the mixed indicator.

Quercetin from Fir and Pine Bark. By E. F. Kurth. *Ind. Eng. Chem.* **45,** 2096 (1953). Dihydroquercetin, present in the heartwood and the bark of Douglas fir and the bark of Jeffrey pine, is readily converted in high yield to quercetin by treatment with hot aqueous bisulfite liquors. Pure crystals of quercetin separate from either hot sodium, potassium, or ammonium bisulfite liquors.

Circular Paper Chromatography. IV. Quantitative Determination of Amino Acids. By K. V. Giri, A. N. Radhakrishnan and C. S. Vaidyanathan. *J. Indian Institute Sci.* **35,** 145 (1953). The method for the quantitative determination of amino acids separated by circular paper chromatographic technique is described. It is based on the elution of the color of ninhydrin stained bands of amino acids separated on the chromatogram with 75% ethanol containing copper sulfate and comparing the color intensity with that of known standard solution of amino acid run on the same paper. The effect of metallic ions, concentration of ninhydrin reagent different solvents for the reagents, temperature, time of incubation, and the area of the bands of amino acids, on the color intensity on the bands of amino acids was investigated. Optimum conditions for an accurate quantitative procedure were established.

Preservation Problems. By W. Hausam. *Das Leder* **4,** 25 (1953). Recently, chlorinated phenolic products have been advocated for the preservation of raw hides but all are not effective. For example, pentachlorophenol is good for controlling wood-destroying fungi but is not effective against hide bacteria. The properties of the more important members of this group of chlorinated phenols were determined using both known germs and germs from raw hide. For testing, all products were dissolved with potassium castor oil soap in order to avoid strong alkalies and differences in alkalinity. The phenol coefficient was determined by the Rideal and Walker method. In addition to the phenol coefficient the bacteriostatic or fungistatic action was also measured by finding the concentration of disinfectant required to stop growth. For the phenol coefficient test the germs are in the test solution only a short time then are transferred to a disinfectant-free medium, whereas in the bacteriostat test they are kept in the solution of disinfectant for a long time. Against Staphylococcus aureus the following phenol coefficients were found: phenol (in soap solution instead of water), 1.25; orthochlorophenol, 6.25; parachlorophenol, 6.25; o-p-dichlorophenol, 25; metacresol, 4.16; orthochlorometacresol, 17.5; parachlorometacresol, 30; o-p-

dichlorometacresol, 87.5; xylenol (m.m'sym.), 3.75; orthochloroxylenol, 25; parachloroxylenol 30; and o-p-dichloroxylenol, 68.8. Similar results were found with Bct. pyocyaneum, with the exception that the highest coefficient was 25 rather than 87.5 because this putrefactive germ, which is abundant in dry sheep and goat skin soak liquors, is quite resistant to chemicals. The results show that germicidal action depends on both the number and position of the chloro and methyl groups. Increasing the number of methyls increased the effect on some bacteria. For example, against Bct. pyocyaneum xylenol was more effective than cresol and the latter was more effective than phenol. In general, monochloro derivatives were more effective with the chlorine in the para position than in the ortho position. Dichloro-derivatives had much greater killing power than monochloro derivatives. The very great decrease in activity of the trichloro and pentachloro derivatives was surprising; solubility and increased molecular size are involved.

Results on known bacteria can not necessarily be applied to practical work such as soak liquors of dry or salted hides. Soak liquors contain a mixed flora and also hide protein which binds part of the chemical and so decreases its germicidal action. In the present tests the disinfectant was not added to the hide or the soak liquor. A skin was soaked then removed from the liquor and the latter used in the germicidal tests. A dry goatskin was soaked 4 days at 25-30° without change of water and a calfskin was soaked 2 days at this temperature with 2 changes of water to remove salt. The goatskin liquor contained 56 million bacteria per cc. and the calfskin liquor 45 million. This is a far greater number of bacteria than are present at the start of a normal soaking and they were all in optimum growth when the disinfectant was added for the test. The dichloro derivatives of phenol and cresol had pronounced germicidal activity but dichloroxylenol was poor. The trichloro and pentachloro derivatives and paranitrophenol had little germicidal action. Parachlorometacresol (Raschit) was better than dichlorometacresol. The best product tested was Raschitol, a combination of halogenated phenol homologs and other materials; it has greater activity than the sum of the activities of its components. The bacteriostatic actions of monochloro and dichloro derivatives of phenol and cresol were good and approximately equal. Trichloro and pentachloro phenols and chlorinated xylenol were poorer. Against mold (penicillium) in 3 days Raschitol, trichlorophenol, ortho-oxydiphenyl and dichloro-metacresol had high fungistatic action. In 16 days the fungistatic action of Raschitol was highest, followed by dichloro-metacresol, parachloro-metacresol, trichlorophenol and ortho-oxydiphenyl. For preserving hides Raschitol was satisfactory in every respect. It preserved hides even at abnormal temperatures. Hides treated with Raschitol made leather of better feel, appearance and sorting quality. Raschitol should be applied as a spray to the flesh side of fresh, salt free hides. After 30 minutes the hides should be salted as usual. Spraying the walls and passages of the hide cellar weekly will keep infection at a minimum.

I. D. C.

The Use of Sodium Silicofluoride in Tanneries. By C. C. Kritzinger. *J. Soc. Lea. Trades' Chemists*, **37**, 252 (1953). As stated in previous papers, sodium silicofluoride has proved so valuable for preventing insect damage to hides and skins that it is widely used in South Africa. This paper is a critical examination of published information on the effects of fluorine compounds in tannery practice. The use of sodium silico fluoride in curing or beamhouse processes will probably lead to more fiber splitting than normal. Such splitting need not be harmful and may, in some cases, be desirable. If fresh, or even cured, skins or hides are subjected to prolonged immersion in saturated solutions of silicofluoride, hair loosening and a bated appearance result. Such a procedure has been used on a small scale, replacing liming and bating, giving acceptable leather. It may be concluded, therefore, that the action of silicofluoride is similar to unhairing and bating

and the removal of protein may not be undesirable. Because of its strong antiseptic power, sodium silicofluoride prevents putrefaction during soaking. In general stock so treated shows a slightly higher lime yield than control stock not so treated. While there is a conflict of evidence as to the effect upon leather quality, the weight of the evidence indicates that sodium silicofluoride treatment will not adversely affect quality. The author concludes that the very beneficial effects of sodium silicofluoride in curing and storing, the absence of harmful effects with the possibility of some beneficial effects in the tannery, warrant its use. No mention is made of the effect on glue or gelatine. R. H. T.

Numerous Uses of Monoglycerides in Industry. By H. Bennett. *Rev. Tech. Inds. Cuir*, **44**, 4 (1952). Monoglycerides are manufactured by esterifying glycerin with a fatty acid or a triglyceride. Monoglycerides are nonionic surface-active agents, and serve as emollients for leather. H. B. M.

Determination of the Quality of Rapid and Slow Tanned Sole Leather. By J. A. Sagoschen. *Das Leder* **4**, 37 (1953). A comparison of rapid tanned and long-time tanned sole leathers was made with leathers tanned by the following three tannages—tanning 40 bends by each: (A). Old vat tannage for 12 months, using 8 rockers (coloring liquors) with liquors up to 1.2° Bé. and 3 layers (versatz) with 3.0, 4.0, and 4.5° Bé. liquors of spruce bark, oak bark and valonia. (B). Rapid vat method for 6 months using 8 rockers with liquors up to 3.5° Bé. and 3 layers with spruce bark, oak bark and valonia and 5, 7 and 8° Bé. liquors which included chestnut and quebracho extracts. (C). A 5 weeks, pure liquor tannage using 6 rockers with 2-6° Bé. liquors and 3 suspenders with 8, 9 and 10° Bé. liquors of spruce, chestnut and quebracho. The leathers of each tannage were divided into 4 lots of 10 bends each and the lots were treated by the following methods: (I). No further treatment. (II). Drum retannage for 48 hours in a 10° Bé. liquor, piled 48 hours, tanned 48 hours in a 16° Bé. liquor, piled 48 hours, washed by hand, fixed lightly, again washed, set out, oiled, dried, and rolled. The liquors contained equal parts of spruce, chestnut and valonia. (III). Retanned as II, but after piling 48 hours from the 16° liquor, the leather was put directly, without washing, into a drum with 5 per cent (wrung leather weight) of powdered valonia, then washed, etc. as for II. (IV). Retanned as II, but after piling 48 hours from the 16° Bé. liquor, the leather was rinsed in dilute liquor and dried completely. The dry leather was hung for 4 days in a 23° Bé. liquor of ordinary quebracho at 38° C., rinsed in weak liquor at 38° C., hung in cold (10° C.) water 12 hours with addition of fresh water to maintain the temperature, drummed with 5 per cent powdered valonia, then hung without rinsing in an acid slurry of finely ground trillo for 4 days, after which the mud was rubbed off with an oil emulsion and the leather was dried and rolled. All of the above processes are normal and the leathers did not differ from the usual commercial product. For testing, strips 20 centimeters wide were taken from the neck end of each bend. Leathers of tannages A and B that were not retanned (group I) were firm and of bright uniform color but C was red-brown, flat and tinny. After retannage II, all leathers were firmer but none were brittle. A and B were assuming the character of retan leather. C was improved but not equal to A. Retannage III entirely removed the old pit tannage character of A and B and they resembled rapid tanned leather in color and firmness. Retannage IV changed all 3 types of leather more than was desirable but all were usable although A and B were cracky even after oiling. The analytical results are shown (partly) in the following table in which all results are given on the basis of 14 per cent moisture:

Retannage		I			II			III			IV	
Tannage	A	B	C	A	B	C	A	B	C	A	B	C
Organic water solubles, %	7.2	9.6	10.4	12.9	15.2	16.2	14.6	16.2	16.4	7.9	7.2	8.3
Combined tannin, %	30.6	30.7	31.7	27.2	28.7	31.1	32.4	36.4	38.1	37.8	42.3	40.9
Hide substance, %	46.8	44.3	42.2	42.6	38.7	35.4	34.8	29.6	28.0	36.1	32.4	32.1
Acidity	3.65	3.90	4.80	3.80	4.16	5.45	3.90	4.30	5.02	3.50	3.80	4.84
Specific gravity	1.01	1.08	1.14	1.04	1.13	1.07	1.08	1.19	1.20	1.05	1.13	1.17
Tensile strength	216	247	239	194	242	253	170	215	232	114	222	220
Stretch	19	26	26	14	26	25	16	24	25	10	26	25
Water absorption, 2 hours	25	22	30	20	18	24	16	17	20	18	25	25
Water absorption, 24 hours	48	42	52	41	40	44	40	40	35	48	53	45
Abrasion resistance	1.9	2.2	1.9	1.5	1.8	1.6	1.5	1.4	1.1	1.8	1.5	1.3
Wear resistance, Km/mm.	338	297	266	370	373	372	304	376	413	352	394	380
Degree of tannage	65.4	69.3	75.0	63.9	74.0	87.9	93.0	123	138	105	131	127

The abrasion results were obtained on the Stather-Herfeld machine. They correspond quite well with actual wear results although the values are not entirely parallel. The wear results were obtained with postmen and are expressed in kilometers required to wear away one millimeter of leather. The following conclusions are given: Leather tanned for 12 months in weak liquors (A) wore better than leather tanned for 6 months in concentrated liquors (B) or that tanned for 5 weeks with extracts (C). By a drum retannage (II) all 3 leathers were improved in wear resistance and all then had approximately equal wear resistance. Impregnation (III) brought the extract tannage (C) up to standard and increased its wear resistance so that its wear exceeded that of the other tannages. A dip impregnation in warm, unsulfited quebracho solution improved both analytical and abrasion values, and soluble matter content was near that of vat tanned leather. Vat tanned leather may have its merits but rapid tanned leather of equal quality can be made. Leather with high solubles (III C) may wear better than leather with low solubles (IV C) or even leather tanned by the old vat method (I A). The analytical values characterize the type of tannage quite well but not leather quality. Specifications should not be based on rigid analytical limits but on both analytical values and appraisal. I. D. C.

Different Possible Ways of Using Formate Masking in Chrome Tanning. By W. Wudich. *Das Leder* **4**, 82 (1953). Stabilizing chrome liquors with sodium formate results in more uniform distribution of chrome through the leather, a finer grain, and an area increase that amounts to 4 per cent for cape goatskins. Too much formate makes soft leather; normally not more than 3 mols of sodium formate is used per mol of chromic acid. Formate may be used to attain certain advantages and also to prevent defects. In one case drawn grain appeared suddenly in a two bath tannage of cape goatskins after a year of satisfactory operation. The tannage was as follows Pickle in salt and hydrochloric and sulfuric acids, add bichromate and potash alum through the axle, let stand 2.5 hours, add antichlor (thiosulfate) then 1 hour later add sulfuric acid. After the total tanning time of 6-7 hours the skins were stable to boiling. The drawn grain appeared 20-30 minutes after adding the thiosulfate and was related to a sharp rise in pH from 1.4 to 6.6. Adding the thiosulfate in 10 equal portions instead of all at once did not remedy the defect. There was a sharp rise in pH between the fifth and sixth additions of thiosulfate and at this point drawn grain appeared. By using a pickle containing, in addition to 10 per cent salt, 3 mols of sodium formate per mol of chromic oxide (Cr_2O_3) the defect was corrected. The use of formic acid in the pickle did not prevent drawn grain. In a second case, cracky grain of boxcalf leather was corrected by use of sodium formate. This leather was first tanned in a 33 per cent basic liquor containing 1.6 per cent Cr_2O_3. After leaving 48 hours on a horse it was retanned in a 50 per cent basic liquor containing 1.6 per cent Cr_2O_3. Cracky grain was caused by the high concentration of chrome in the grain layer. A more uniform distribution of the chrome was obtained with formate. In a third case, rough grain in boxcalf leather was corrected by adding sodium formate to the pickle. I. D. C.

The Control of Mold on Leather. By W. Grassmann and P. Stadler. *Das Leder* **4**, 103 (1953). The bacteriological method of testing fungicidal activity was as follows: One cc. portions of fungicide in increasing dilutions were added to 9 cc. portions of sterile beer wort agar culture medium. The prepared medium was then inoculated with one loopful of a dilute spore suspension. To obtain a uniform spore suspension it was necessary to add an anionic surface active agent, for example 0.5 per cent of dodecylsulfate. A more important test is that on leather. For this test a leather must be used that is known to permit mold growth. Pieces 2.5 cm. square, weighing 2.5-3.0 grams may either

be dipped for 1-2 hours in 20-25 cc. of increasing dilutions of the fungicide or the edges of the leather may be waxed and 1 cc. of the test solution applied to the leather surface. The two methods of application gave the same results. The treated leather pieces were hung in individual corked jars containing wet cellulose material. The following day the leather was inoculated with 2 loopfuls of spore suspension. The ability of the fungicide to kill spores was also tested using dry, spore-inoculated, artificial silk threads. The threads were left in the disinfectant for up to 3 hours, then carefully washed and put on beer wort agar. Substances not soluble in water were dissolved by adding small amounts of alkali. Usually the inoculum was Aspergillus niger but results with penicillium and rhizopus were not different. The results were variable; sometimes at one dilution the leather was sterile and at the next dilution there was decided growth and heavy spore formation whereas in other cases there was a gradual increase in growth on dilution but no spore formation until a high dilution was reached. Results are shown in the following table:

	Tested on		
	Culture medium	Leather	Spore test
Sodium fluoride	1000*	100	0
Potassium bifluoride	1000*	500	
Silicofluoride	1000*	100	
Zinc silicofluoride	1000*	100*	
Formaldehyde	1000	100	
Hexamethylene tetramine	1000*	100*	
Corthymol	1000	100	0
Nipacombin	2000	500	0
8-hydroxyquinoline	160,000	100	
Novex	20,000	100*	0
p-nitrophenol	10,000	1000	0
Raschit K	10,000	2000	1000
Raschitol	15,000	1500	
Preventol CMK	10,000	2000	
KM 11	5000	1000	500
dichloro-m-cresol	10,000	1000	0
p-chloro-sym-xylenol	10,000	1000	
dichloro-sym-xylenol	10,000	1000	
Trichlorophenol	40,000	2000	0
Preventol fl 1	40,000	2000	1000
Pentachlorophenol	20,000	2000	100
Preventol O	10,000	2000	
Preventol N fl.	1000	500	
Sch 101	120,000	40,000	75,000

In this table the figures are the greatest dilution (1:100 etc.), on the solution basis, that was effective. Values were also calculated on the leather plus solution basis; they are 3.5 times those shown above. Values followed by a * indicate that the fungicide was not effective at this dilution but that a higher concentration was not tested. In the spore test O indicates no fungistatic action. The acive ingredients of the trade preparations were as follows: Nipacombin, higher molecular esters of p-hydroxybenzoic acid; Novex, 2,2′-dihydroxy-5,5′-dichlorodiphenylsulfide; Raschit K, Preventol CMK, and KM 11, p-chloro-m-cresol; Preventol fl. I, trichlorophenol; Preventol O, o-phenylphenol; Preventol N fl., o-phenylphenol and benzylphenol; Sch 101, organic mercury compound. The leather may

have absorbed the fungicide selectively and therefore contained more than the calculated amounts. Fungicidal activity was much greater by the bacteriological test than on leather. This is especially noticeable for 8-hydroxyquinoline and Novex which were very effective in culture media but practically inactive on leather. On the other hand, Sch 101 was quite effective by all 3 tests. It also was the only substance that was effective except at high concentrations or after long time of action. Sch 101 involves the question of mercury poisoning; however compounds such as phenyl mercury borate are in use that have been found to be entirely nonpoisonous to higher animals. The ideal fungicide for leather has not yet been found. This work has not touched on the problems of permanence of treatment or the development of tolerance by fungi. I. D. C.

The Determination of Sodium Silicofluoride in Hide Salt and in Hides. By K. Rosenbusch. *Das Leder* **4**, 108 (1953). Sodium silicofluoride has been in use for some time in South Africa for curing hides. The recognition and determination of this salt in raw hides, glue stock or gelatin is important because of a possible fluorine content of edible gelatin.

Qualitative tests in the absence of organic matter. (a) *Water drop test.* Treat a little of the hide salt with concentrated sulfuric acid in a platinum or lead crucible, warm over a small flame, then hold a drop of water in a platinum loop over the crucible. If silicofluoride is present in the salt, volatile silicon tetrafluoride will form, then will decompose to form silicic acid in the water and turn it cloudy.

(b) *Crawl test.* Warm a little of the material to be tested (e.g. salt) with 2 cc. of of sulfuric acid in an unused reagent glass, shake and observe how the acid drains from the glass surface. If silicofluoride is present, hydrofluoric acid will form and wet the glass after which the sulfuric acid will drain from it like water from a greasy surface.

(c) *In the presence of organic matter* the above tests may fail and the following very sensitive test of Feigl should be used. Treat finely divided hide material with 1 cc. concentrated sulfuric acid in a platinum crucible. Lay on the crucible a filter paper on which one drop of molybdate solution has been put. Warm gently until white fumes of sulfur trioxide appear, but acid must not splatter onto the paper. Spot with a drop of benzidin and develop over ammonia. A blue color forms if silicofluoride is present. The solutions required are (a) ammonium molybdate solution made by dissolving, cold, 15 grams $(NH_4)_2MoO_4$ in 100 cc. water then adding 35 cc. nitric acid of density 1.2 (the nitric acid may be omitted to advantage according to the author's results); and (b) benzidin solution made by dissolving 0.05 grams of the base in 10 cc. concentrated acetic acid then diluting to 100 cc. If the sample contains strong reducing agents such as sulfide it must be ashed, then treated with 0.5 gram of powdered silica (SiO_2) and 2 cc. sulfuric acid before testing.

Quantitative Methods in absence of organic matter. (a) *Gravimetric determination* of silica (SiO_2). To an amount of salt containing about 0.4 grams of sodium silicofluoride in a platinum crucible, add 1.2 grams of boric acid solution and evaporate to dryness. This will remove the fluorine as BF_3. When cool add 25 cc. of water, make alkaline, acidify with 5-6 cc. hydrochloric acid and determine silica by the usual method.

(b) *Volumetric method.* If alkaline substances such as bicarbonate or sodium salts of organic acids are absent the sodium silicofluoride can be titrated with sodium hydroxide solution to the red color of phenolphthalein. 1 cc. 0.1*N* NaOH = 3.6 mg. H_2SiF_6 = 4.7 Na_2SiF_6.

Quantitative Method with organic matter present. The hide or leather can not be ashed without loss of fluorine so it must be finely divided by rasping or grinding. Put 2-3 grams of material in a 100 cc. Claisen type distilling flask provided with separatory funnels in the neck and side arm and a thermometer in the neck extending into the liquid.

Add 25 cc. of 10 normal sulfuric acid and heat in an oil bath. At 110° heavy foaming will start and should be controlled by addition of water sparingly, from the funnel in the side arm. When the foam subsides in a minute or two, heat to 140° and maintain this temperature within 5 degrees for 2 hours by adding water from the funnel in the neck at the same rate as that at which it distills. After 2 hours raise the temperature to 155-160° and distill for 15 minuees more. Sulfur trioxide forms but does not interfere with the determination. Make the distillate up to 500 cc. and titrate 50 cc. first with 0.5*N* NaOH to the dimethyl yellow end point then boil, add phenolphthalein, and titrate hot to the end point of the latter. From the last titration calcuate the silicofluoride as follows: 1 cc. 0.5*N* NaOH = 7.2 mg. H_2SiF_6 = 9.4 mg. Na_2SiF_6. In a trial with sodium silicofluoride and hide powder 99.2% of the silicofluoride was recovered. Pietzka and Ehrlich [*Angewandte Chemie* **65,** 131 (1953)] have described a method for determining fluorides as the lead bromofluoride, PbBrF, and a volumetric method for small amounts of fluorine by titration with thorium nitrate-alizarin solutions. I. D. C.

Investigations on Fur Dressing and Fur Improvement. VI. Influence of Bleaching of Natural Colored Fur Skins on the Properties of the Hair and of the Fur Leather. F. Stather and G. Königfeld. *Ges. Abhandl. Deut. Lederinst. Freiberg/Sa.* **7,** 5 (1951). Fur bleaching usually involves several steps: (1) treatment with dilute Na_2CO_3 or NH_4OH ("killing"), which facilitates the penetration of the bleaching agent by swelling the hair and perhaps attacking the surface membrane; (2) mordanting with $FeSO_4$; (3) bleaching with H_2O_2 in slightly alkaline solution; and (4) removal of Fe by treatment with oxalic acid. This series of treatments always weakens the hair and skin to some extent. The purpose of these tests was to determine the effect of each step, and of variations in concentration, time, temperature and pH value, on the degradation of hair and skin. Degradation of hair was estimated from increase in solubility in dilute Na_2CO_3, increased digestability by pancreatin, and decrease in tensile strength, and degradation of skin was estimated from loss in tensile strength only. Material used was rabbit skin, tanned with HCHO, pickled by the Leipzig process, and oiled by hand. All tests were made with 100 g. pelt per liter of solution, and concentrations are expressed in g. per liter. The alkali pretreatment had no appreciable degrading action on hair or skin, whether the alkali was NH_4OH, Na_2CO_3, or NaOH (all at pH = 11.5), and whether the Na_2CO_3 concentration was 5 or 20 g. per liter. Omission of this pretreatment did not lessen the degradation after bleaching, but addition of HCHO to the alkali bath improved the strength after bleaching quite markedly. The $FeSO_4$ treatment, in itself, had little deteriorating effect, but degradation after bleaching increased with concentration of $FeSO_4$ previously used. No satisfactory bleaching effect was obtained without pretreatment with $FeSO_4$, even when the time of bleaching was doubled, but the concentration of $FeSO_4$ should not exceed 10 g. per liter. $Fe_2(SO_4)_3$ and $CuSO_4$ did not catalyze the H_2O_2 bleach and $CuSO_4$ damaged the hair and skin badly. Deposition of basic Fe salts on surface of the hair must be avoided, as the Fe must penetrate to the pigment granules. Addition of $NaHSO_3$ to the $FeSO_4$ bath improved the subsequent bleaching action, but addition of $(NH_4)_2C_2O_4$ or $(NH_4)_3PO_4$ did not, though all three compounds made it easier to remove Fe in the final step. Damage to hair and skin occurred chiefly in the H_2O_2 treatment, and increased markedly with time, temperature, pH value and concentration of H_2O_2. So did the bleaching effect, up to a certain maximum. The least damage, along with satisfactory bleaching, was attained by bleaching with 30 ml. of 30% H_2O_2, at 20°C., for 1 hour at pH = 5 and then 2 hours at pH = 8. Addition of Avirol (a sulfated fat) or sulfated castor oil to the bleaching bath did not lessen the damage to hair or skin, but did improve the bleaching action. Addition of alleged protective agents, "Egalisal" (a protein decomposition product) or "Protektol" (a lignosulfonate derivative) did not diminish the damage

to hair. Protektol did lessen the damage to the skin, but also lessened the bleaching action. Tests with NH_4OH, Na_3PO_4, and Na_2SiO_3 as alkalinity regulators in the bleach bath were favorable to Na_2SiO_3. Attempts to bleach fur skins with $NaHSO_3$ and with $KMnO_4$ were unsuccessful, and the latter damaged the hair and the skin. H. B. M.

The Recovery of Pigskins. The So-called Dresden Scalding Process. By W. Hausam. *Das Leder* **4**, 132 (1953). The Dresden process is as follows: Bleed immediately after killing; scald at 60°C. using a sensitive temperature regulator in the vat, a temperature above 60.5° is not permissable; the hog must go at once into the scalding vat; each hog must remain in the vat only long enough (4-5 minutes) to loosen the hair so it will come out with the scraper without effort. The process is based on the theory that hog skin retaining the animal heat is more resistant to hot water than the cooled skin. Stather [*Gesammelte Abhandlungen* No. 8, 12 (1952)] has criticized the method but based the criticism on work with small pieces of salted hide washed overnight in cold water. The process has been used successfully on 5932 hogs and the skins compared with 3065 skins from unscalded hogs. The following typical values were found from tests on vegetable tanned leather made from opposite sides of the same animal, the skin on one side of each animal having been scalded and that on the other side not scalded: Stretch 32, 29%; strength 183, 184 Kg./cm^2; tear 174, 159 Kg./mm^2 for scalded and unscalded resp. Scalded skin is thus found to be equal or superior to unscalded skin. I. D. C.

The Effect of Kind of Tannage, Intensity of Tannage, and Oiling of Leathers on Their Tensile Strength and Stretchability. F. Stather and K. Schmidt. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.* **7**, 66 (1951). In these experiments, the tensile strength (T.S.) and % elongation at break (Str.) was measured for strips of dehaired, delimed steer hide, and for similar strips tanned or otherwise treated in various ways. The results for the tanned strips are given as percentages of the values of T.S. and Str. obtained for the untanned wet hide. Tests were made on the wet strips, and on air-dry strips. Each test was made on 20 random strips, all from the butt and back area of one hide split to uniform thickness. Treatments, and their effects on T.S. and Str. were as follows:

Treatment	Tensile strength		Strength at break	
	Wet	Dry	Wet	Dry
None (dehaired hide)	100	65	100	37
Alcohol dehydration	92	58	71	66
Pickling	61	62	70	67
Sulfur tannage	64	71	69	64
Alum tannage	75	50	60	51
Chrome tannage	84	55	66	49
Vegetable tannage	88	43	44	30
Syntan tannage	84	40	48	22
Formaldehyde tannage	74	26	77	27
Quinone tannage	78	50	67	57

All the treatments *reduced* T.S. and Str. for the wet strips, and all but the so-called S tannage reduced T.S. for the dry strips, while the effect on Str. of the dry strips varied with the treatment—increased by alcohol dehydration, pickling, and tannages with S, alum, chrome, and quinone; decreased by vegetable, syntan, and HCHO tannage. Further tests showed

that varying the amounts of fixed alum, chrome, HCHO, and vegetable tannin (within rather narrow limits e.g., Cr_2O_3 2.5-4.6%, degree of vegetable tannage 54-66) had little effect on T.S. or Str. Treatment of the strips with grease, variously applied, had a marked effect, as indicated below.

Tannage	Oil Application	% Fat	Tensile Strength		Stretch at break	
			Wet	Dry	Wet	Dry
None	none	0.4	100	—	100	—
Chrome	none	0.5	88	62	76	57
	fat liquor	6.3	108	96	99	90
	hand stuffed	20.3	107	99	99	83
	burned in	34.4	—	68	—	90
Vegetable	none	0.3	71	41	50	30
	fat liquor	0.7	70	50	50	36
	hand stuffed	11.4	80	62	47	56
	burned in	28.4	—	55	—	51

Application of grease to chrome leather raised T.S. and Str. for wet strips to values equal to, or even exceeding, those for the untanned hide, and raised T.S. and Str. for dried strips to values approaching those for the wet untanned hide. Application of grease to vegetable tanned leather had a smaller effect. The reduced effect of grease applied by burning in, even though much more grease was added, is noteworthy. Comparison of values for non-oiled leathers of the same tannage, in the two tabulations, indicates rather poor reproducibility. H. B. M.

Resin Tannage with Methylol Compounds of Nitrogen-Containing Bases. H. Herfeld. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.* **7**, 80 (1951). In resin tannage, the nitrogen base (urea, thiourea, or melamine) is reacted with HCHO or other aldehyde to form H_2O-soluble monomeric methylol compounds. The skin is impregnated with these monomers, which are then polymerized by the action of acid or heat, forming insoluble compounds that are deposited in, and perhaps combined with, the skin. The author first determined the conditions under which the maximum percentage of the methylol compound is precipitated. In salting out experiments with dimethylol urea and various additions of HCl, maximum precipitation by saturated NaCl was about 75%, at pH values slightly under 2, in 24 hours, and very little more in 48 hours. Only 25% was precipitated at pH values slightly under 3. At the lower pH values 80-85% of the precipitate formed without the addition of salt, in 48 hrs., but the presence of salt did increase the rate of precipitation. Extensive precipitation tests were carried out by mixing the base (urea, thiourea, or melamine) with different amounts of HCHO and HCl, digesting at either 18 or 35°C. for periods up to 24 hours (urea) or 72 hours (thiourea, melamine), filtering, determining nitrogen in the filtrate and calculating by difference the percentage of the initial base that was precipitated. For urea, precipitation in 24 hours increased with decreasing pH value, was slightly greater for the monomethylol compound (2 g. urea: 1 g. HCHO) than for the dimethylol compound and was more rapid, though, no more complete at 35 than at 18°. Maximum precipitation was 82%. In a second series, in which urea : HCHO was varied from 1 : 0.3 to 1 : 1.2 (by weight), all at pH = 1.9, maximum precipitation (87%) was obtained with urea : HCHO = 1 : 0.6, slightly more HCHO than corresponds to the monomethylol compound. For thiourea the results were much the same, except that precipitation at 18° was much slower, requiring 72 hours for

around 90% completion. Maximum precipitation occurred with thiourea : HCHO = 1 : 0.55, corresponding to a mixture of nearly equal parts of mono- and dimethylol compound. For melamine, maximum precipitation occurred at pH = 5.5 and decreased very markedly at higher and lower pH values. Precipitation increased with increasing ratio of HCHO to melamine up to the tetramethylol compound, and was substantially constant for higher ratios. Maximum precipitation (72 hours) was 88%. Combining value tests were made with hide powder, to see whether these precipitation values corresponded with fixation of resin by hide. In general they did. Combining values up to 97 (urea, 24 hours), 122 (thiourea, 48 hours, and 120 (melamine, 48 hours) were obtained. With urea and thiourea, it is unnecessary to form the monomer before adding the tanning agent to the skin. Any two of the three components—nitrogen base, HCHO and HCl—can be added first, and the third component added after the collagen is impregnated with the first two. This does not hold for melamine, where the monomer must be preformed by brief heating of melamine and HCOH, followed by rapid cooling. Tanning tests were made on goat and calf skins, after normal beamhouse treatment. Unusual opening up by prolonged liming or bating is unnecessary, and produces looseness. Tanning is done in a short float (80-90%), in liquor containing 7-8% NaCl. Recommended quantities are 10-12.5% urea and 6-7.5% HCHO, or 8-12.5% thiourea and 4-7% HCHO, or 8-12% melamine and 8-14% HCHO. The stock is milled several hours, or over night, then brought to pH = 2 (urea or thiourea) with HCl or H_2SO_4, or to 4.5-5 (melamine), and run 24-48 hours. The sock is washed, and neutralized to pH = 4.5 (urea or thiourea), washed, and processed in the usual way. Shrinkage temperatures are 75-80°C. (urea and thiourea) or 80-90° (melamine). The leathers are pure white, perfectly light-fast, resistant to action of acid and alkali, and can be dyed with most acid or direct dyes. The fullness varies with the amount of resin given. The chief failing of these leathers is an extraordinarily high and rapid water absorption. The resins themselves, apart from skin, absorb several hundred per cent of water, the absorption increasing with number of methylol groups. Absorption of water by the resins is not lowered by drying at 100°C. Urea or thiourea leather can be retanned with chrome, but not vice versa, because of the low pH value of the resin tannage; however, Cr leather can be retanned with melamine. A light urea-HCHO pretannage results in better fullness, especially in thin areas, after Cr normal tannage. Or a light Cr retannage can follow a heavier urea-HCHO pretannage, thereby saving Cr. There is no reaction between cationic Cr and the resin. Resin-tanned leather can be retanned with vegetable tannins or syntans, but not vice versa, because tannins precipitate the resin. The advantage of a resin pretannage, before vegetable tannage is saving of time. If plump leather is desired, the salt content is reduced, and the acid is added along with the urea to give an acid plumping—the HCHO being added last. Such resin-pretanned vegetable leathers do not absorb water abnormally, since the active groups of the resin combine with the tannin. H. B. M.

XXIII

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